Design and Synthesis of New Liquid Crystalline Materials

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von

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I offer my sincere thanks to Prof. Dr. M. Mazik for agreeing to be the co-referee of my thesis.

I would like to add a very special note of appreciation to my wife, Amber, for her support, enduring patience and for putting up with my seemingly endless weeks of work, hours in front of the computer, and the inconveniences and lost weekends.

I wish to acknowledge the financial support for this work from the state of Lower Saxony.

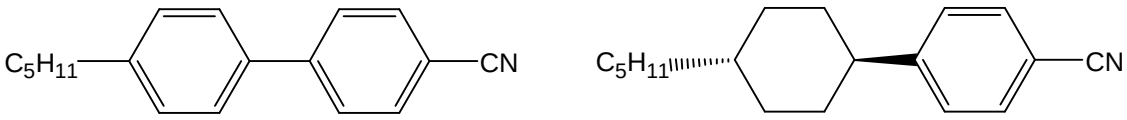
To my parents and my wife

Contents

Introduction

The term liquid crystal covers a wide area of systems. There are thousands of papers concerned with the chemical structures, physical properties and technical applications of liquid crystals. Most important chemical structures include rod-like molecules, disc-like molecules, amphiphilic materials, cellulose derivatives, metallomesogens, steroids, gylcolipids etc. and from their typical applications, liquid crystal displays, surfactants, membranes, colour pigments, advanced materials and photoconductors are the most important ones. Liquid crystals are often thought of as 'exotic', but they are omnipotent in research and daily life.

The broad application of LCDs became feasible when, in 1971, the twisted nematic cell was invented by Schadt and Helfrich.[1] At the early 1970s Gray and co-workers[2] synthesised the first chemically and photochemically stable crystal that exhibited a nematic phase at room temperature (**1**, Scheme 1). Another commercially important new class of materials, also with a nematic phase around ambient temperature, the cyanophenylcyclohexane (**2**, Scheme 1) were introduced by Eidenschink[3] in 1977. Researchers systematically utilized the melting point depression of mixtures of these and similar materials[4-7] and made it possible to produce twisted nematic (TN)-LCDs with a reasonable working temperature range and long life time.[8]



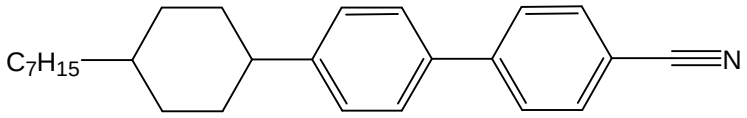
1 **2**

Scheme 1. First commercially stable LC with a nematic phase around room temperature

Over the past years liquid crystal displays have become increasingly important in information technology. In 1999, more than two billion LCDs were produced worldwide.[9] For all applications improved performance of the displays is continuously required i.e. wider viewing angles and enhanced brightness, lower driving voltage and less power consumption, faster response time and reduced manufacturing costs etc. and there has already been carried out substantial work in this direction.[10-14] However, there is still a growing need for more and more new materials to be synthesised and tested for their LC properties.

1.1. Calamitic liquid crystals

Substances forming calamitic mesophases have been know for more than 100 years but only recently, rapid advance in active matrix liquid crystal display (AM-LCD) technology helped these materials to achieve the crucial position in flat panel display technology they hold today.[15] Structure **3** shows a typical calamitic liquid crystalline material.

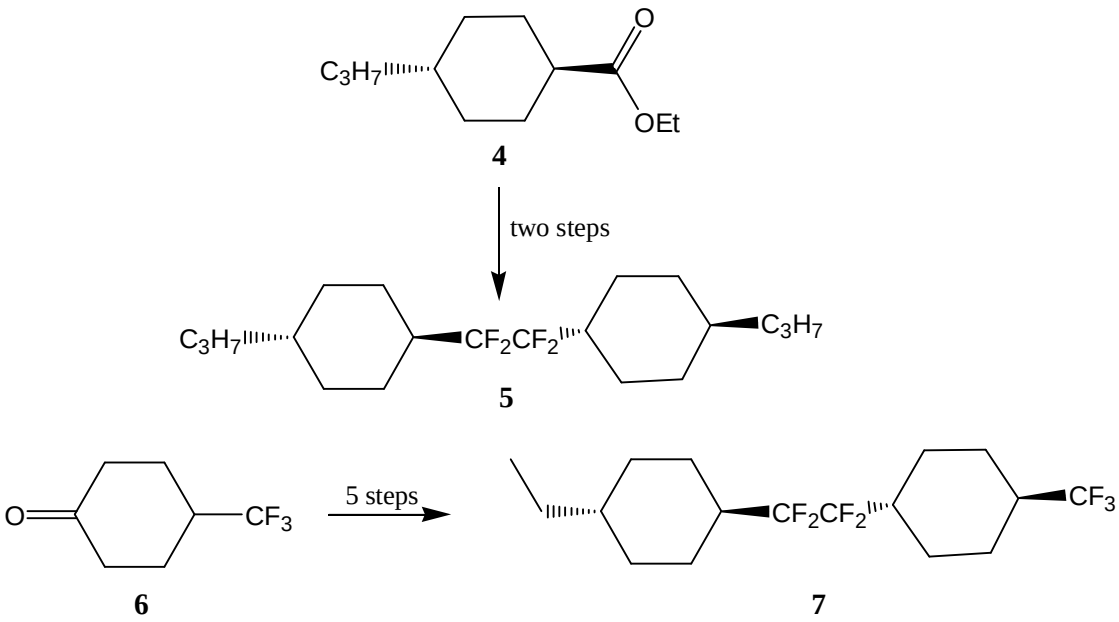


3

The liquid crystals used in twisted nematic (TN) and super twisted nematic (STN) display devices are calamitic liquid crystals. A number of such liquid crystals have been synthesised and used in practical displays.[16-17] The major disadvantages with these types of devices are the narrow and non-uniform viewing cone which affects their performance. The use of multidomain technique,[18] the introduction of an optical compensator to reduce the amount of light leakage in the dark state,[19] use of an electrical field parallel to the plane of the substrates,[20] use of amorphous twisted nematic liquid crystals,[21] and various modification in the calamitic liquid crystals with phenyl bicyclohexyle moiety,[22-26] enhanced and optimized their performance.

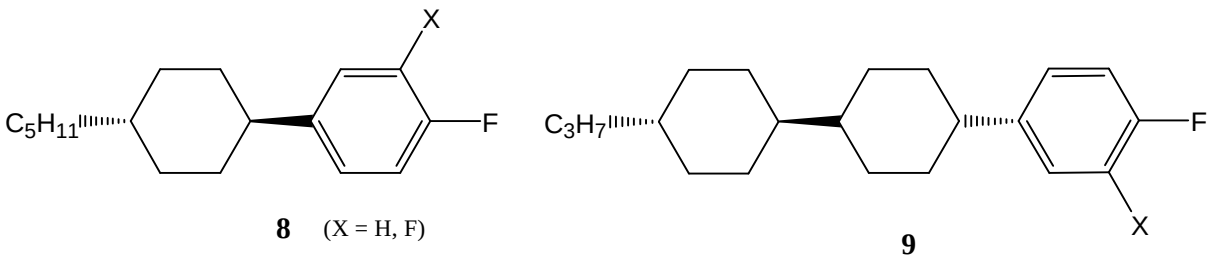
Much of the materials research in the LC field is characterized by a trial-and-error approach based on empirical structure-property relationships. For example the switching behaviour of nematics for display applications is basically governed by their rotational viscosity (γ_1). So, during design of liquid crystals for display applications, various items with regard to their rotational viscosity have to be taken into account. It is know that there is an empiric monotonic relation between the size of a molecule and its clearing point i.e. a 4-ring LC with a nematic phase will almost always exhibit a higher clearing point than a corresponding 2-ring material and also the higher the clearing point of the material, the higher is the corresponding rotational viscosity which results in quite slow switching properties ultimately increasing power consumption of the display. So, materials with low rotational viscosity are desirable.

Various modifications in the basic cyclohexyl, bicyclohexyl and phenyl bicyclohexyl structures have been made recently to overcome problems of electrooptic and viscoelastic parameters. Kirsch et al.[26] showed that by perfluorination of the central ethylene link in bis (cyclohexly) ethane derivative resulted in dramatic increase of the clearing temperatures (Scheme 2).



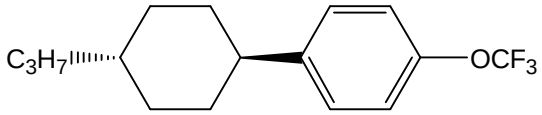
Scheme 2. Synthesis of symmetrically (**5**) and unsymmetrically (**7**) substituted bi-(cyclohexyl) tetrafluoro ethane derivatives.

Fluorinated ring materials like **8** have rotational viscosities far lower which become interesting as mixture components in order to reduce the switching time of the display. In **9** the lateral fluorination is effective for increasing the value of dielectric anisotropy by three to four times but, on the other hand, decreasing the clearing temperatures by 30 to 40 K for each lateral fluorine substituent.[27]



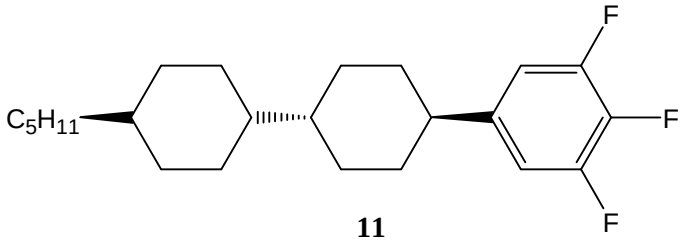
Scheme 3. Fluorinated two (**8**) and three ring (**9**) materials

Materials with terminal trifluoromethoxy group such as **10** play a central role in commercially used standard AMD liquid crystals mixtures. Such materials possess higher clearing temperatures allowing the operating temperature range for LCDs to be extended to higher temperatures.



10

It has also been demonstrated that the insertion of a difluorooxymethylene bridge into a specific location of the mesogenic core structure of phenylbicyclohexyl-type liquid crystals **11**[28] results in a class of materials like **13**[29] that exhibit surprising improvements like broader nematic phase, a higher dielectric anisotropy, a lower rotational viscosity but also a higher specific resistivity and voltage holding ratio (Scheme 4).



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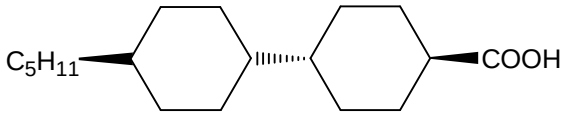

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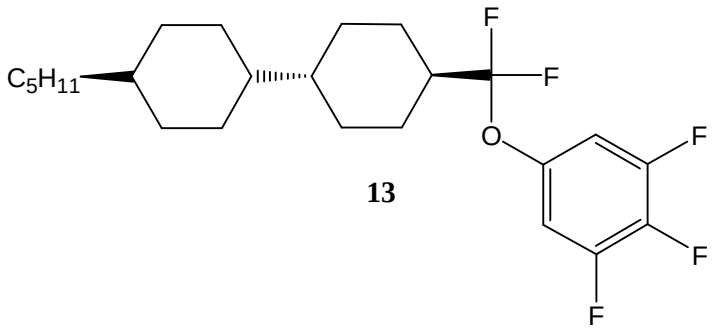
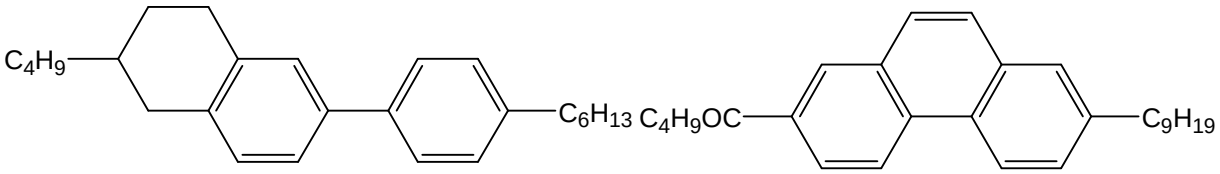


13

Scheme 4. LC material with difluorooxymethylene bridge

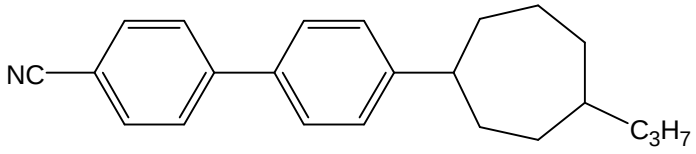
1.2. Materials having ring system with more than six atoms

Materials with ring systems containing more than six atoms often have high clearing temperatures but usually show relatively large viscosities. Compounds like **14**[30] and **15**[31] display a larger breadth than oligophenyl compounds which reduces their mesogenity in comparison to the later.



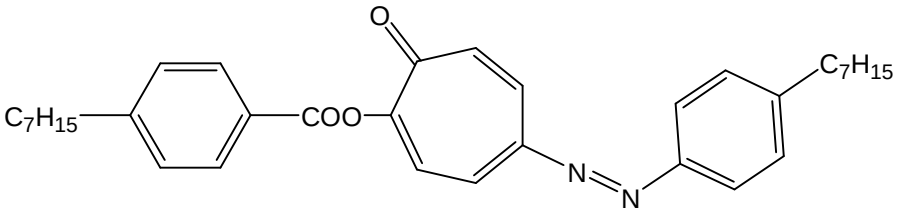
14 **15**

In the last 10 years a very large number of different ring systems have been investigated for liquid crystalline properties. Many of them are not very effective in terms of their mesogenity. In seven-membered rings like **16**,[32] the directions of the substituent bonds are not parallel, leading to a bent molecular shape.

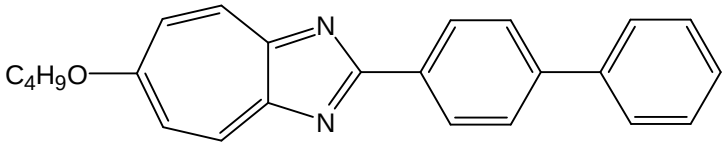


16

Compounds **17**[33] and **18**[34] are additional examples of materials with seven-membered ring systems. These materials show smectic and nematic textural features perhaps due to a more linear nature indicating that mesogenic properties are possible in materials having other than six-membered ring systems provided that these materials produce linearity in shape concerning their terminal groups.



17 Cr. (SmI 80 SmC 86) N 142 I



Cr 211 (SmA 207) N 240 I

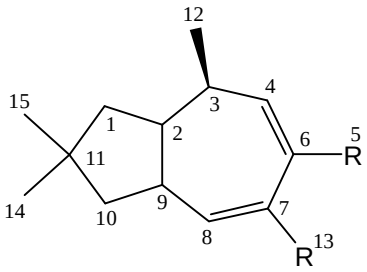
18

It is clear from the ongoing discussion that by modification of the basic structures a wide range of change of properties affecting the liquid crystal behaviour of these materials can be produced. However, there is still a need for the synthesis of increasingly structurally diverse materials to be investigated for their LC behaviour and to be explored for their structure-property relationships allowing novel solutions of problems in LC research. One way of course, is the trial-and-error approach but molecular modelling could in principle provide a better approach to predict the key properties of the target molecules before the actual synthesis is undertaken. This could save an enormous amount of cost and effort.

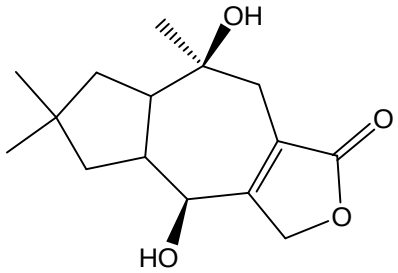
1.3. Substituted azulenes/hydroazulenes

A number of azulene derivatives are known with varying substitution patterns[35] and researchers are still engaged in synthesising more derivatives for mechanistic studies. 2,6-Disubstituted azulenes and perhydroazulenes also constitute parts of many natural products and are expected to be potentially photo-chromic compounds.[36] It is also surprising that the crystal structures of only a few azulenes and their derivatives have been reported.[37] It is also important to note that the substitution pattern of azulene and perhydroazulene derivatives plays an important role in determining the properties described above and specific substitution at position 2 and 6 which gives linearity for these molecule is the most important parameter regarding their properties as liquid crystals.

The hydroazulene skeleton occurs widely in nature. Sesquiterpenes belonging to the lactarane family such as velleral (**19a**), vellerolactone (**19b**) and lactaroruffin (**20**) represent an interesting variation of the perhydroazulene skeleton in natural products. Over a dozen of such compounds have been isolated from Basidomycetes.[38]

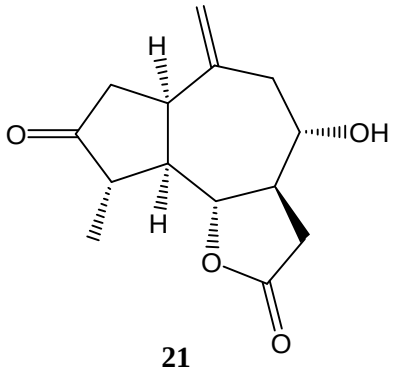


19a $R^5 = R^{13} = CHO$
19b $R^5 = CO$, $R^{13} = CH_2O$



20

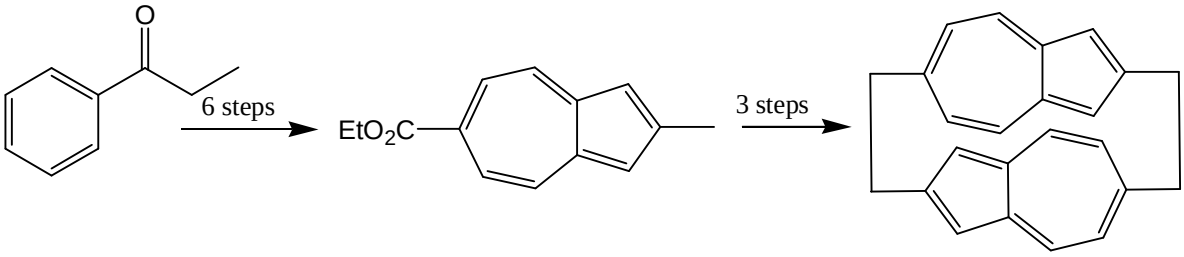
The widespread occurrence[39] and the broad range of biological activities[40] of perhydroazulene natural products, ranging from diuretic and anti-inflammatory to antitumor, combined with their structural diversity makes them interesting synthetic targets.[41] From the synthetic view point the conformationally flexible seven-membered ring represents an even more demanding challenge than the usually conformationally more well behaved six-membered ring. Furthermore, it is rather difficult to construct the *cis*-fused perhydroazulene skeleton as in grossheimin (**21**).



21

A search of the chemical literature revealed that different synthetic strategies have been employed to construct the azulene and subsequently perhydroazulene skeleton. Luhowy et al.[42] synthesised the 2,6-disubstituted azulene **23** which later was coupled to the azulenophane **24**. The synthetic strategy includes cyclization of **22** by a Mannich reaction followed by carbene addition on a reduced aromatic system and ring expansion to yield **23** which on hydrolysis and subsequently ion exchange column chromatography resulted in **24**.

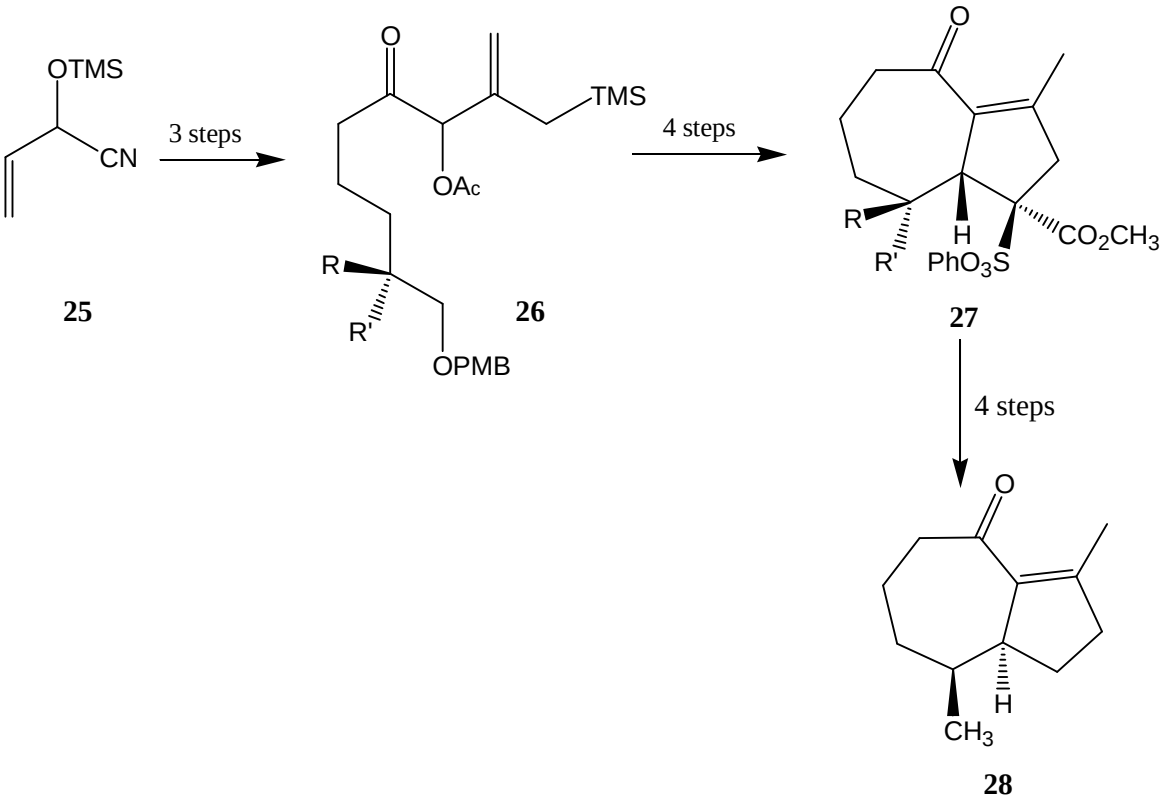
Since in charge transfer complexes, azulene normally acts as the π-donor, forming charge transfer complexes with many acceptors, it was tried to measure the intramolecular charge transfer activity between the two azulene nuclei of **24**.



22 **23** **24**

Scheme 5. Synthesis of the azulenophane **24**

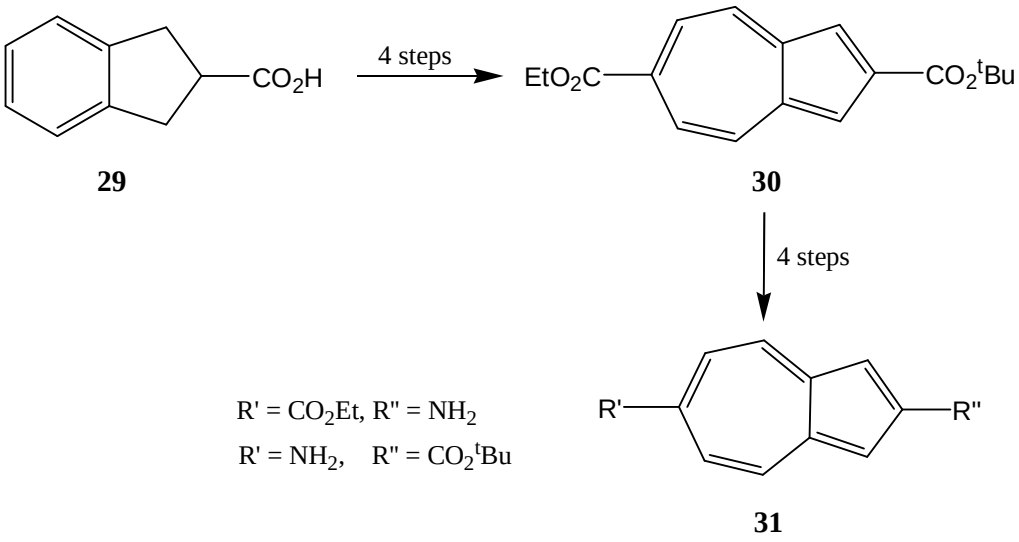
Several strategies involving metal catalyzed coupling reactions for the synthesis of substituted perhydroazulenes are also known. Trost et al.[41] used one of such strategies where a stereo-controlled intramolecular Pd-catalyzed trimethylenemethane (TMM) cycloaddition was employed for the synthesis of perhydroazulene derivative **28**. Although in principle this constitutes a facile protocol for the synthesis of perhydroazulene derivatives, to achieve a desired substitution pattern, like the one mentioned above, is again a demanding challenge.



25 **26** **27** **28**

Scheme 6. Asymmetric synthesis of the perhydroazulene derivative **28**.

Zindel et al.[43] synthesised red coloured 2,6-disubstituted push-pull aminoazulene carboxylates **31** from 2,6-azulenedicarboxylate **30**, a key compound in the synthesis and which was prepared in four steps from 2-indancarboxylic acid. The effect of push-pull substituents on the azulenes were analyzed by NMR and UV/Vis spectroscopy.



Scheme 7. Synthesis of push-pull azulenes **31**

As mentioned earlier, 2,6-disubstituted azulenes and perhydroazulenes are potentially important precursors for new LC materials and are hence important synthetic targets. Regarding these azulenes, two pathways have been recognized, starting from 2-indancarboxylates as mentioned above or from 5-substituted tropolones.[44] In 1951 ring expansion of indans was reported to give 2,6-substituted azulenes, but only in very low yields.[45] Later, Keehn et al.[42] improved this approach by using reduced indans followed by a dehydrogenation sequence (see above). At about the same time suitable tropolone precursors in reaction with cyanoacetates were used for the synthesis of 2,6-substituted azulenes.[46] Although various routes for the synthesis of perhydroazulenes exist (see above), specifically 2,6-disubstituted are not easily accessed and a synthetic protocol giving satisfactory yields of 2,6-substituted perhydroazulenes with a minimum number of steps would be highly desirable.

1.4. Aim of this study

The above discussion clearly demonstrates the great importance of the azulene and perhydroazulene skeletons especially those substituted at 2 and 6 positions. It is also clear that varying the number of cycles and substitution patterns can have a dramatic effect on the mesomorphic properties of the new materials in hand. However, efforts have never been made to use fully reduced 5,7-fused ring systems to synthesise new LC materials. So, it was supposed that the replacement of cyclohexyl or phenyl ring by the perhydroazulene ring system from a typical biphenyl cyclohexyl or bicyclohexyl phenyl system or construction of entirely new columnar system with perhydroazulene ring would result in a change of mesomorphic properties of the materials formed. This would, of course, constitute a new entry into the calamitic liquid crystals not known so far.

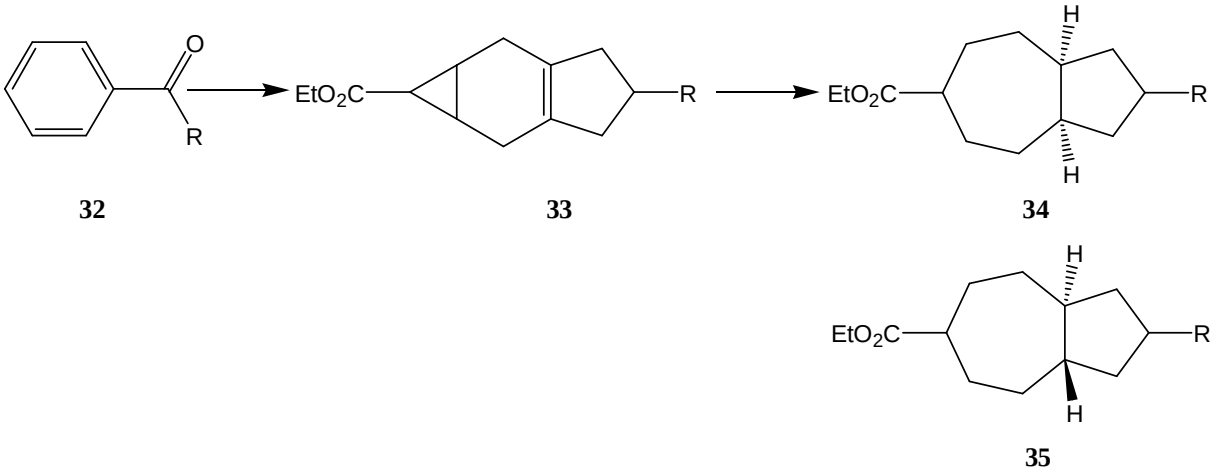
As viscosity parameters play a key role in switching time of a LCD, it was supposed that new materials with perhydroazulenes as a core unit would exhibit a dramatic change into their rotational viscosities.

In the foregoing part of this chapter some basic information about liquid crystals and their structure-property relationships has been discussed. Some details about the importance of azulenes and perhydroazulene derivatives as a basic skeleton in many natural products have also been mentioned. In the present work a novel synthetic route to *cis* and *trans*-fused perhydroazulenes and their various derivatives will be discussed. Some of the new materials were also investigated for their liquid crystalline properties.

1.4.a 2, 6-Disubstituted perhydroazulenes

It is known that the variation in the main core of a liquid crystal and also in the terminal groups results in a change of various mesomorphic properties. It is also important to note that the stereochemistry plays an important role in determining the structure-property relationships of these materials. Most of the calamitic liquid crystals known so far consist mostly of six membered rings as core units with various alkyl chains as well as polar moeities as terminal groups. There is no report so far, of the use of perhydroazulenes as core units in LC materials and since perhydroazulenes constitute a part of many natural products, it was also important to investigate their stereochemical aspects in greater detail. The first part of this work reports the synthesis and stereochemical aspects of various 2,6-disubstituted perhydroazulenes. The synthetic route started with alkyl phenyl ketones **32** which were

transformed by a Mannich reaction and Birch reduction of the 2-alkyl indan product followed by a carbene addition to the terminal double bond resulting in **33**. This, by ring enlargement followed by hydrogenation yielded 2,6-substituted perhydroazulenes **34** and **35** where R is an alkyl chain with 3 to 5 carbon atoms (Scheme 8).

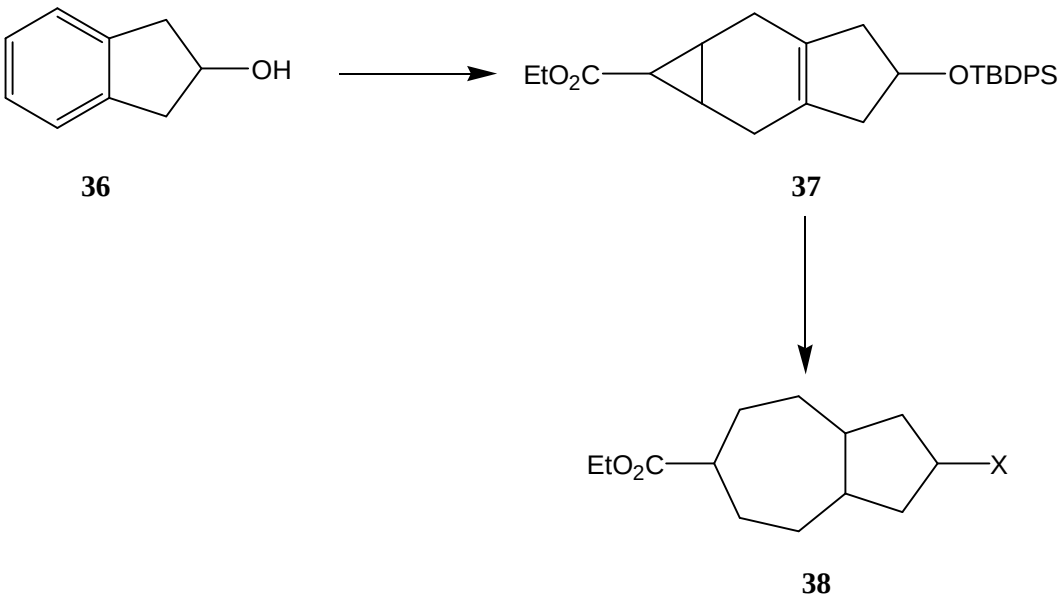


32 **33** **34**

35

Scheme 8. General route to various *cis,trans*-fused perhydroazulenes

It is evident that in perhydroazulenes, the chain extension at position 6 is quite straightforward, whereas, to extend the chain at position 2, repetition of the whole synthetic sequence would be required. Therefore, another synthetic route to perhydroazulenes was needed with the possibility of modification at position 2 of the fused system of perhydroazulenes. A synthetic route leading to this started from 2-indanol **36** which by Birch reduction followed by protection of hydroxyl group by a butyl diphenyl silyl group and subsequent carbene addition on the terminal double bond resulted in **37** which finally by ring enlargement followed by hydrogenation yielded **38** where X is either hydroxyl or halogen providing an opportunity of modification at position 2 of the new system (Scheme 9).

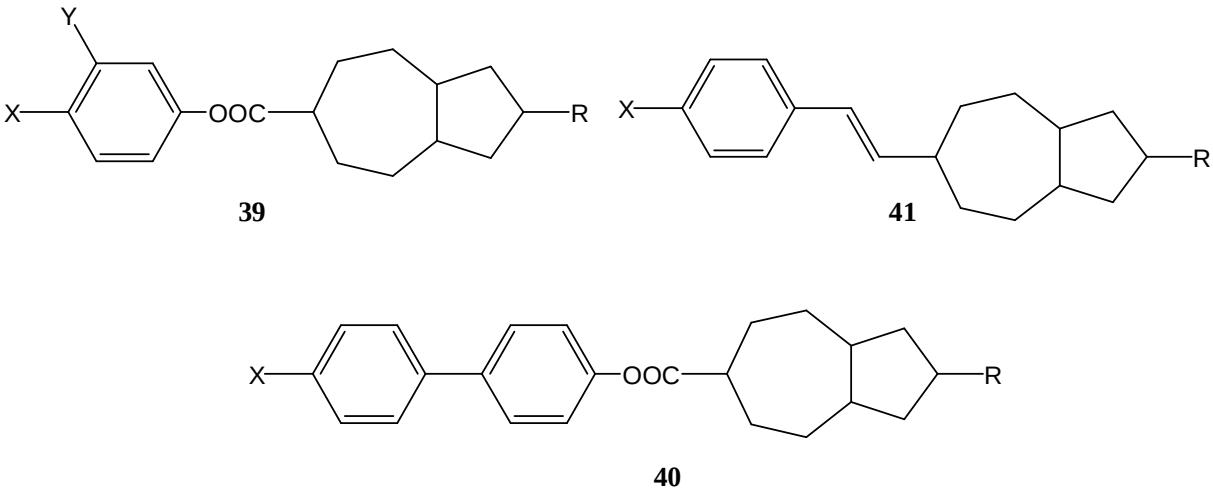


36 **37** **38**

Scheme 9. Synthetic route to various 2-substituted perhydroazulenes 6-carboxylate

1.4.b Derivatives of 2, 6-substituted perhydroazulenes

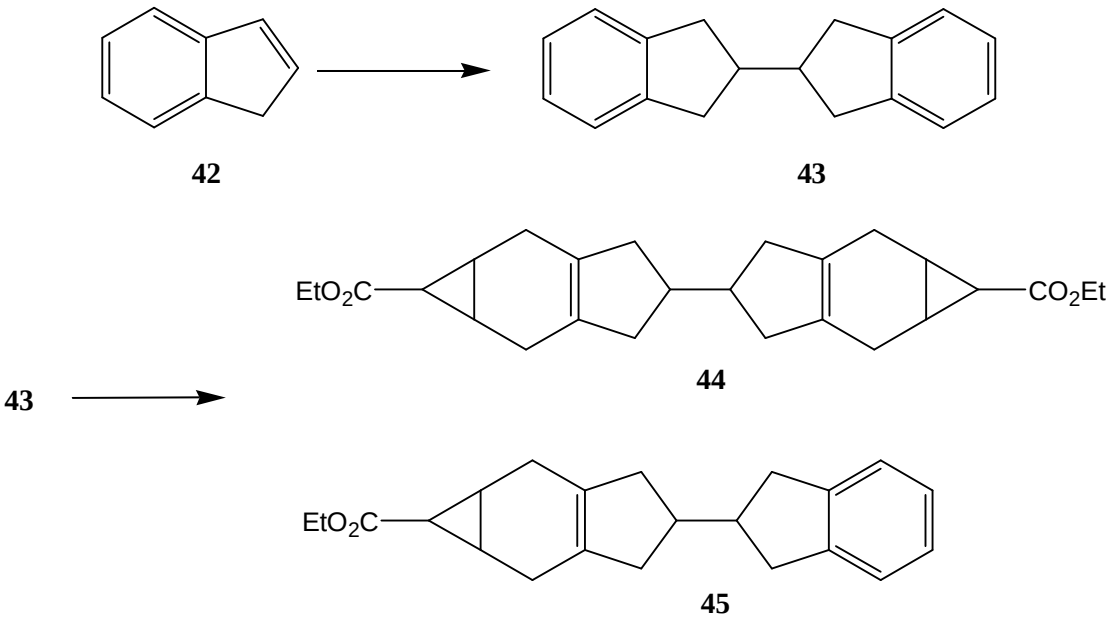
Materials with rod like or longitudinal structures belong to the category of calamitic liquid crystals and again the change of core units or terminal groups results in a change of mesomorphic properties. It is thus extremely interesting to discover, whether or not the new materials with various ring systems like 5/7 and with various terminal polar and nonpolar groups could show or alter the mesogenic properties. Hence, it is necessary to synthesise simple model materials with new ring systems first and then correlate the chemical structures with their mesogenic properties. The second part of this work is based on the synthesis of various derivatives of the above mentioned perhydroazulenes in order to investigate the enthalpies of phase transition and textural features of the new materials formed. The synthetic route leading to the synthesis of various derivatives of perhydroazulenes like **39**, **40**, and **41**, involved transesterification of the above esters, reduction followed by Wittig coupling to get system like **41**, halogenation at position 2 followed by Friedel-Crafts coupling where X and Y represent polar end groups such as CN, F while R indicates various alkyl groups, phenyl, hydroxyl as well as halogens (Scheme 10).



Scheme 10. Various perhydroazulenes derivatives

1.4.c Bisindan

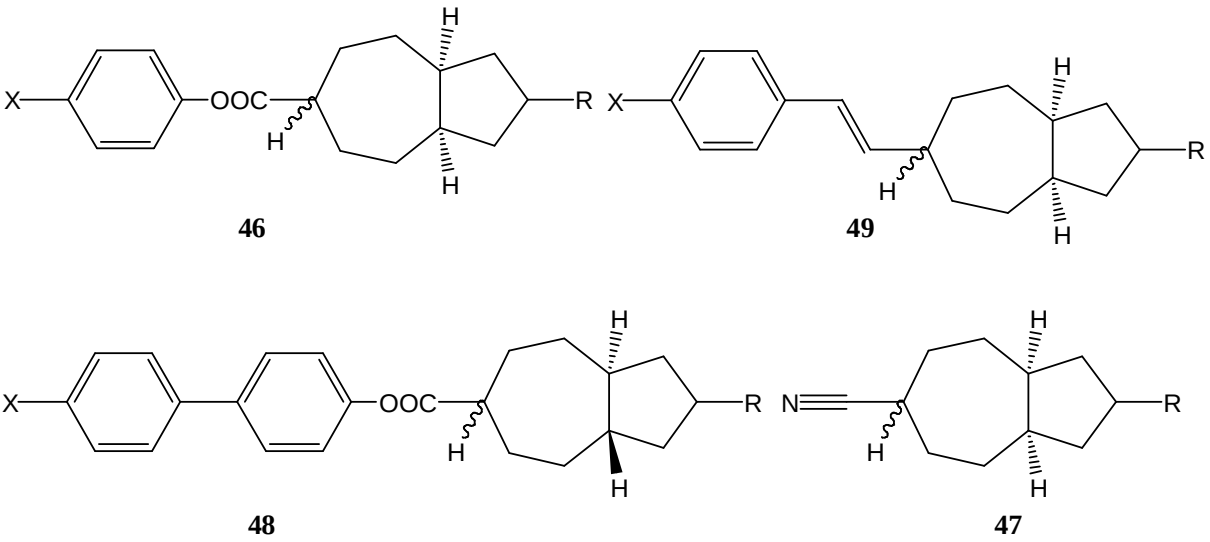
The third part of this study consisted in the dimerization of indene **42** with lithium naphthalenide to the bisindane **43** and then proceeding by the same strategy as mentioned above, (Birch reduction of the aromatic system of the bisindane and carbene addition to the external double bond), various synthetic intermediates such as **44**, **45** and their corresponding acids were obtained. These intermediates and further materials synthesised therefrom are also supposed to have novel mesomorphic properties. The stereochemistry of the bisindane at position 2 and 2' was investigated by employing density functional theory (DFT) of Becke, Lee, Yang and Parr (BLYP) in connection with the 6-31 G (d) basis set as implemented in the Gaussian program, and then by its single crystal X-ray structural determination.



Scheme 11. Routes to bisindane **43** and its derivatives

1.4.d Mesogenic properties of the materials based on perhydroazulene ring systems

Despite of being a part of many natural products, the perhydroazulene ring system has never been investigated for its mesogenic properties. As discussed above it could well be an alternative to the existing cyclohexyl or bicyclohexyl based calamitic LC materials. In this part of the present work, all newly synthesised materials were investigated for their textural features. The thermal behaviour of the materials was investigated by polarizing microscopy and by differential scanning calorimetry. Materials such as **46** and **47** with *cis*-fused ring system, **48** with *trans*-fused ring system as well as materials with olefinic linkage such as **49** were also investigated.



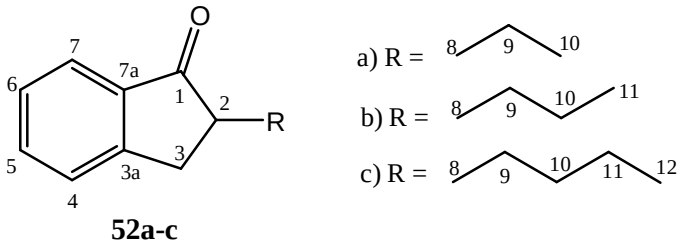
Scheme 12. Materials with novel mesomorphic properties

2. Results and discussion

2.1. Synthesis of *cis,trans*-fused ethyl 2-alkyl perhydroazulenes-6-carboxylates

2.1.1. 2-Alkyl-indan-1-ones 52a-c

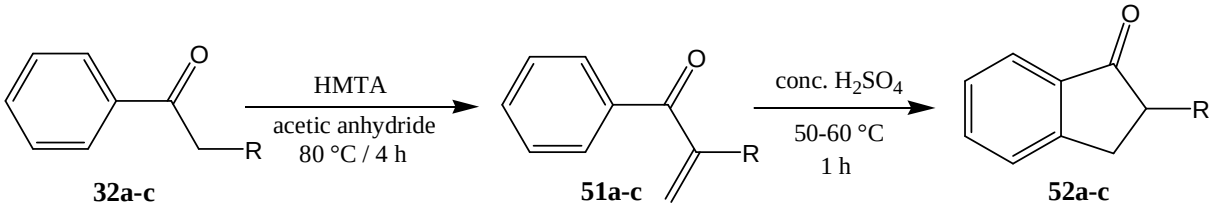
As mentioned in the previous chapter the mesogenic properties of LC materials depend upon the core molecule as well as on the terminal groups, therefore various perhydroazulenes ring systems with different alkyl groups at position 2 were synthesised. The synthetic route started from the of 2-alkyl-indane-1-ones **52a-c** as starting materials for new LC materials.



52a-c

Scheme 13. 2-Alkyl-indane-1-ones **52a-c**

The synthesis of the 2-alkyl-indane-1-ones **52a-c** began with a Mannich type reaction of various alkyl aryl ketones. There are many reports[47] for the synthetic utility of the Mannich reaction for the preparation of 2-alkyl-1-indanones. However, due to an often lengthy procedure and poor yields, we used the procedure of Bhattacharya et al.[48] which employs hexamethylenetetramine as Mannich base, resulting in a simple procedure with satisfactory yields. A mixture of various commercially available alkyl aryl ketones **32a-c**, hexamethylenetetramine and acetic anhydride was heated at 80 °C for 5 h under nitrogen atmosphere followed by aqueous work-up and produced the acrylophenones **51a-c** which were not isolated and directly underwent acid-catalyzed cyclization (H_2SO_4, 50-60 °C) to produce the corresponding indanones **52a-c** in good to excellent yields (67-88 %, see details in experimental section). All of the derivatives **52a-c** were characterized by their usual spectroscopic and analytical data mentioned only partly in the literature[59] but detailed data can also be found separately in the experimental part.

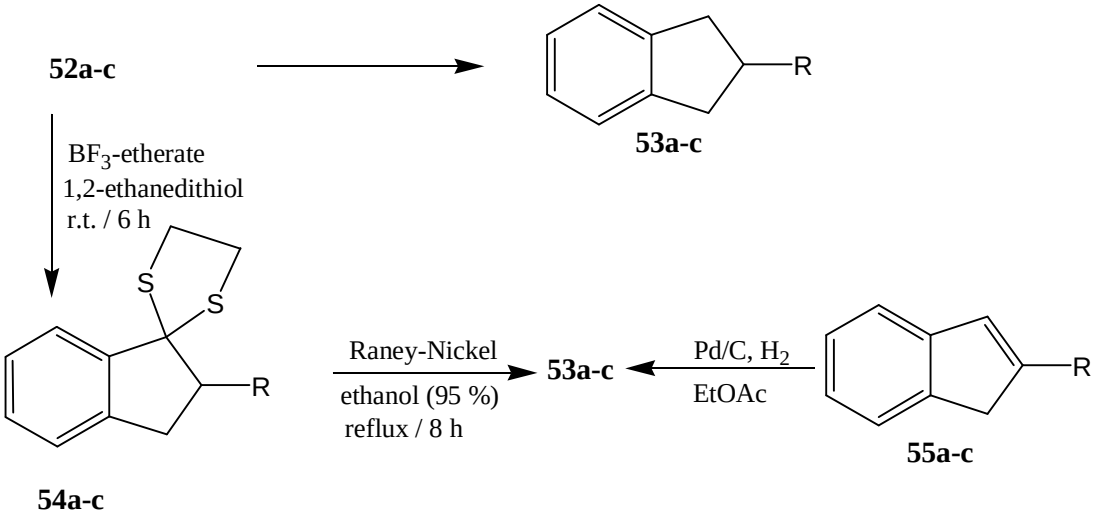


32a-c **51a-c** **52a-c**

Scheme 14. Synthetic route to the aromatic ketones **52a-c**

2.1.2. 2-Alkyl-indans 53a-c

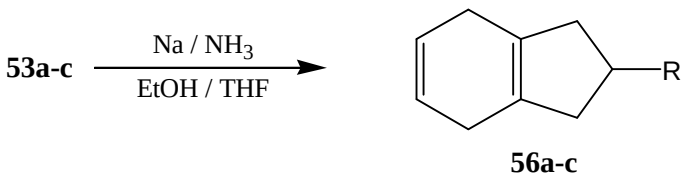
In the next step the carbonyl group of **52a-c** was reduced in order to get the hydrocarbon **53a-c**. At first the Clemmensen reduction with amalgamated zinc and then catalytic reduction[50] with hydrogen in the presence of acid was tried, both approaches resulting in poor yield. Later, the procedure of Mitra et al.[51] was employed where the carbonyl group is first protected with 1,2-ethandithiol in the presence of BF_3-etherate for 6 hours at room temperature to yield the thioketals **54a-c**. Reductive desulphurisation with Raney-nickel in ethanol finally resulted in **53a-c**. Sometimes in addition to **53a-c**, indene derivative **55a-c** were also produced. These by further catalytic hydrogenation in the presence of Pd/C were converted to **53a-c** in quantitative yields (see details in experimental section).



Scheme 15. Synthesis of 2-alkyl-indans **53a-c**

2.1.3. Birch reduction of 53a-c

Birch reduction[52] of 2-alkyl-indans **53a-c** was carried out in liquid ammonia in the presence of sodium metal in dried ethanol and THF to provide the 2-alkyl-4,7-dihydroindanes derivatives **56a-c** in almost quantitative yields (see details in experimental section). It is important to note that **56a-c** were not stable enough at room temperature and slowly oxidized back to **53a-c**, so they were immediately used for further reactions.

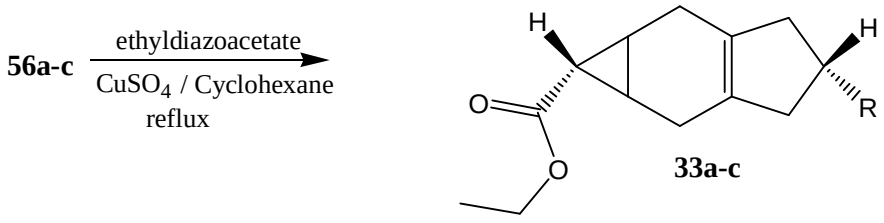


Scheme 16. Birch reduction of **53a-c**

All derivatives from **53** to **56a-c** were characterized by their usual spectroscopic and analytical data which can be found separately in the experimental part.

2.1.4. Cycloheptatrienes 59a-c

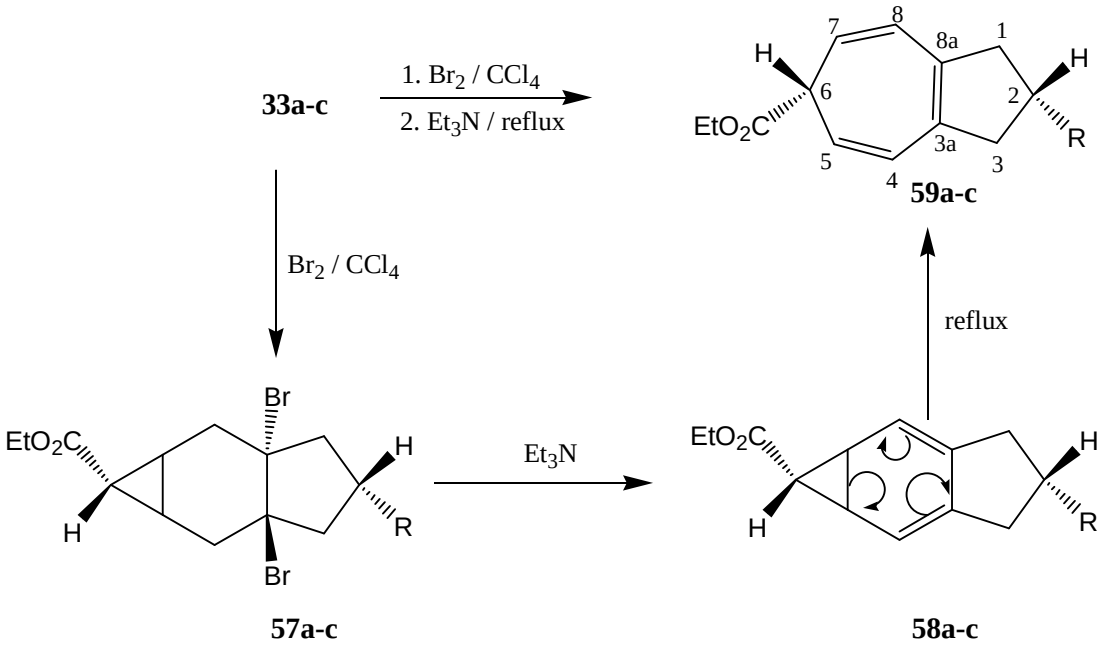
Continuing the synthesis, **56a-c** were treated with ethyl diazoacetate[53] and a copper catalyst ($CuSO_4$) in refluxing cyclohexane to afford carbene adducts **33a-c** in good yields (54-64 %, see details in experimental section). The addition of ethyl diazoacetate in the refluxing mixture of **56a-c** in anhydrous cyclohexane and copper catalyst resulted in higher yields when the time of addition was increased. The higher yields as in **56c** with its long carbon chain at position 2 could be due to the repulsive effect for the carbene addition to the inner carbon double bond in spite of the fact that the central carbon double bond is more electron rich and hence more susceptible for such additions. Compounds **33a-c** were found to contain impurities with almost similar retention factor which could be separated by chromatography on a silver nitrate impregnated silica gel column with pentane as an eluent with increasing polarity by dichloromethane. The column was prepared according to the procedure of Li et al.[54] The column was packed in the same way as an ordinary silica gel column and wrapped with dark paper (wrapping with dark paper is not necessary for flash chromatography). For good separation, 50 g of adsorbent for each gram of mixture was required. Compounds **33a-c** were obtained as colourless liquids which solidified below 0 °C. The disappearance of a broad singlet due to the protons of the outer double bond in **56a-c** and appearance of small coupling constant of 4.33 Hz between the protons on the cyclopropyl ring, presence of a quartet at 4.1 ppm due to methylene protons of the ester group indicated that structures of **33a-c** had formed. However, final confirmation of the stereochemistry of all these structures was assured from the X-ray data of their corresponding acids (see later).



Scheme 17. Synthetic route to **33a-c**

The next step involved the ring opening of **33a-c** to the cycloheptatrienes **59a-c**. The carbene adducts **33a-c** were first treated with bromine[42] in carbon tetrachloride resulting in *in situ* formation of the dibromides **57a-c**. After complete addition of bromine, triethylamine was

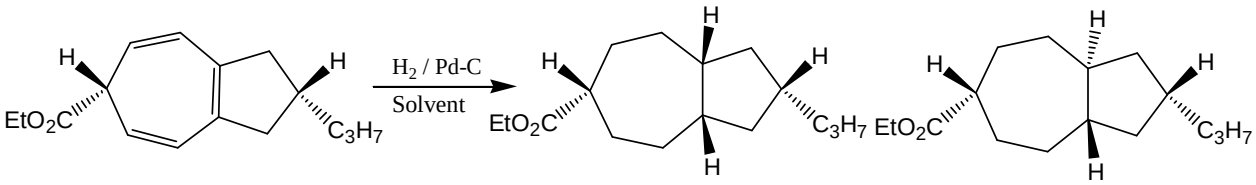
added slowly which resulted in the formation of salt of triethylamine-hydrobromide and *in situ* formation of the norcaradiene intermediates **58a-c** which by overnight refluxing caused the formation of **59a-c** as light bluish coloured liquids. The compounds **59a-c** were again contaminated by small impurities which were separated with a silver nitrate impregnated column of silica gel with pentane and dichloromethane as eluents as mentioned in case of **33a-c**. The pure **59a-c** were again a mixture of two isomers as clearly indicated by the presence of overlapping ^{13}C signals. It was possible to separate one of the two isomers with a silver nitrate impregnated column, as eluting first from the column; however, the second isomer could not be obtained in pure form as it was always contaminated with small amounts of the first isomer. The presence of a multiplet at 2.67 ppm in ^{1}H NMR for 6-H, doublets at 6.17-6.21 ppm with the coupling constant 9.1 Hz for 4/8-H and a singlet at 141.8 ppm in ^{13}C NMR for C-3a/8a indicated the formation of **59a-c**; the spectroscopic data did not allow the confirmation of the exact nature of the second isomer. However, it is likely that they differ due to the different orientation of the terminal groups at position 2 and 6 in **59a-c**. The position of the double bonds as well as orientation of the terminal groups in one of the isomers of cycloheptatriene **59a-c** was confirmed later by the X-ray structures of the acids **70** and **72** (Figures 5, 7), assuring the stereochemistry in **59a-c**. Detailed spectroscopic and analytical data of **59a-c** can be found separately in the experimental part.



Scheme 18. Synthesis of cycloheptatriene derivatives **59a-c** (R = alkyl)

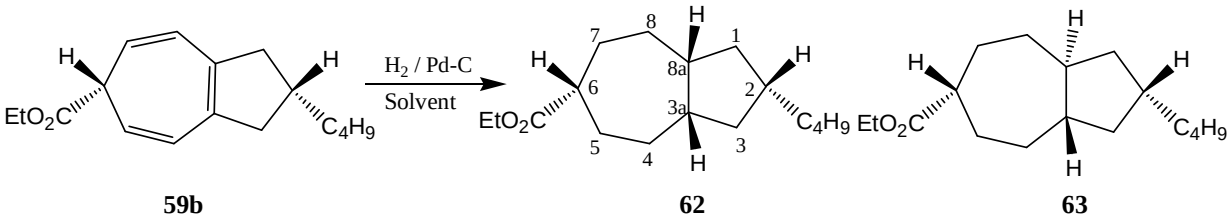
2.1.5. *cis,trans*-Perhydroazulenes

In the final step of the formation of *cis,trans*-fused perhydroazulenes, the precursors **59a-c** were hydrogenated. Catalytic hydrogenation of **59a** by using Pd/C in EtOAc resulted in a mixture of two isomers **60** and **61**, clearly indicated by GC and NMR spectra. The isomer mixture was separated by column chromatography. Due to almost the same polarity of both isomers, it was a tedious job to elute the column using pentane as an eluent whose polarity had been slightly increased by the addition of dichloromethane (1-10 %). The separation of these isomers still took many hours.



Scheme 19. Hydrogenation of **59a**

In case of the butyl derivative **59b**, hydrogenation yielded compounds **62** and **63** which were separated in the same way as described for **60** and **61**.

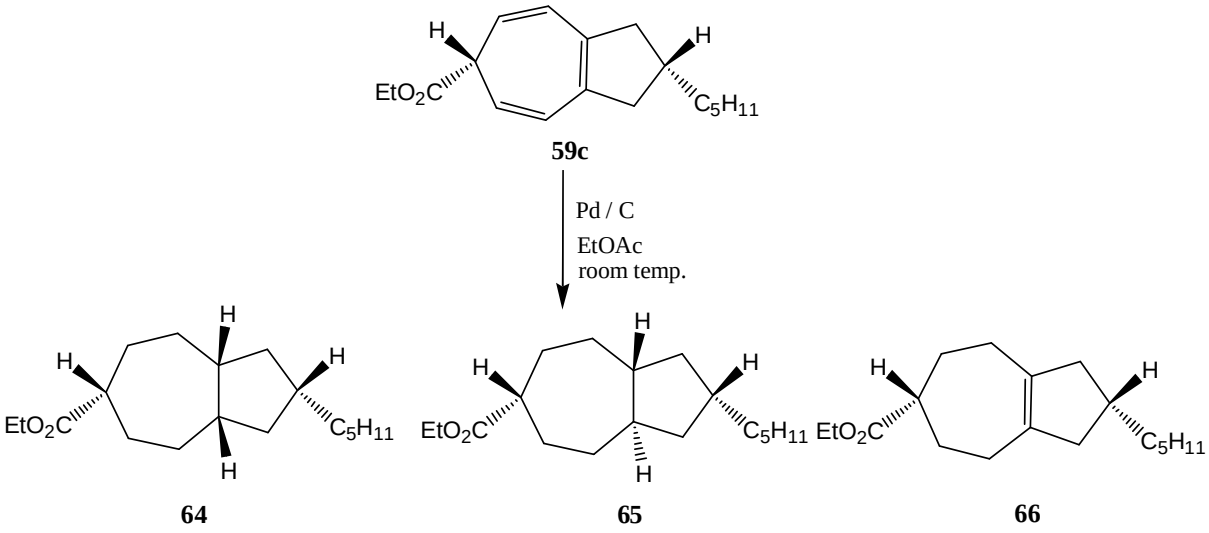


Scheme 20. Hydrogenation of **59b**

It is important to note that the *cis*-isomer in all cases was found to be less polar than the *trans*-isomer although not by a large margin and it was possible to obtain the pure *cis*-compound in appreciable quantity (> 60 %) from the mixture. However, the completely pure *trans* isomer could not be obtained, as it was contaminated with traces of the *cis*-isomer in all cases. After complete characterization of **59a-c** by their usual spectroscopic, analytical and X-ray data (see below), it was possible to elucidate the structures of fully hydrogenated azulene systems **60-63**. The disappearance of doublets at 6.1 ppm with coupling constants of 9.1 Hz for the 4/8 protons in **59a-c** and appearance of multiplets for these protons was indicative of the formation of **60-63**. Further confirmation of the structures of all these

derivatives was provided by the 2D NMR data coupled with various analytical data which can be found separately in the experimental section. The shown stereochemistry of the *cis*-fused systems was confirmed by the X-ray structures of the acids **73** and **74** (see later).

Following the same procedure as described for **59a** and **59b**, **59c** was hydrogenated in the presence of Pd/C under hydrogen in order to get the perhydroazulene systems **64** and **65**. In case of the propyl **59a** and butyl **59b** derivatives, respectively, the hydrogenation always resulted in completely reduced products. However, in the case of **59c**, hydrogenation with Pd/C in EtOAc at room temperature yielded in addition to **64** and **65**, the partially reduced ester **66** also. The formation of **66** was not expected, however, it was considered to be an important side product having a double bond at the ring junction and thus avoiding the problem of *cis,trans*-isomerism at this position. The formation of **66** can possibly be explained by considering the steric effect of the long pentyl chain at position 2 which resulted in slow hydrogenation at room temperature. Hydrogenating **59c** at an elevated pressure and for a longer time resulted in completely reduced systems. The elucidation of the structure of **66** was performed by NMR spectroscopy and MS analysis as **64/65** gave molecular ion peak at 280.3 while the peak for **66** was at 278 and the disappearance of ^{13}C signal for C-3a/8a for **64/65** at 42.96 (2 x d) and appearance of this signal for **66** at 135.85 (2 x s) was indicative of the formation of **66**, although later 2D NMR spectra confirmed the structure of **66**. As the stereochemistry in case of **60** and **62** was established from the X-ray structures of their respective acids, the stereochemistry in case of **64-66** was also supposed to be the same as described for **59c**. The complete spectroscopic data of **64-66** can be found in the experimental section again.



Scheme 21. Hydrogenation of **59c**

2.1.5.1. Effect of various factors on the *cis,trans*-isomer ratio of the perhydroazulenes

As the pure isomers were required for further synthetic work, various hydrogenation methods were investigated in order to get exclusively one isomer. There are numerous reports[55] on the catalytic hydrogenation of C-C double bonds over Pd/C and the problem of controlling the stereochemistry of the reduction product and of minimizing *cis,trans*-isomerism. Platinum is found to be an excellent choice to give the *cis*-adduct while palladium often yields the *trans*-product. We studied the effect of different solvents and reducing agents on the formation of the *cis*- and *trans*-isomers as we were more interested in having exclusively one isomer. It was found that in most of the cases the ratio of *cis,trans*-isomers remained 4:1 and exclusively one isomer could not be obtained (Table 1).

Reducing agent	**Solvent**	**Substrate / temp. °C**	**Pressure (atm)**	**% *cis*-isomer**	**% *trans*-isomer**
10 % Pd / C	EtOAc	**59a** / r. t.	< 1	70	30
10 % Pt / C	EtOAc	**59a** / r. t.	< 1	72	28
10 % Pt / C	AcOH	**59a** / r. t.	< 1	70	30
10 % Pt / C	EtOH	**59a** / r. t.	1	74	26
PtO_2	EtOAc	**59a** / r. t.	< 1	86	14
PtO_2	EtOAc	**59a** / r. t.	1	75	25
PtO_2	EtOH	**59a** / r. t.	< 1	85	15
PtO_2	EtOH	**59a** / 0	< 1	85	15
PtO_2	Cyclohexane	**59a** / r. t.	1	70	30

Table 1. Effect of various factors on the *cis,trans*-isomer ratio

It is worthwhile to note here that the reduction of the indan ring followed by the addition of a carbene was found to be an improvement on the Buchner[56] method and can be used as general route to a variety of novel substituted perhydroazulenes.

2.1.5.2. Molecular mechanics calculation on *cis*/*trans*-fused perhydroazulenes systems

A rational basis for an energy comparison of isomers consists in computational modelling of their potential energy hypersurfaces. From the available various methodologies for energy calculations, a force field method (Merck FF)[57] was selected as a compromise between reliability and computing time. The perhydroazulene system can exist in one or more of the stereo-isomers listed in figures **a-h** on the next pages. Therefore, efforts were focused to find

out the most stable stereoisomers on the basis of the theoretical calculation of their steric energies leading to thermodynamic stabilities as a starting point for the discussion. By employing the molecular mechanics approach, energies for stereoisomers **a-h** were calculated; the results are also given in figures **a-h**.

The first prefix always refers to the stereochemistry of the ring junction, the second to the stereochemistry of the five membered ring (orientation of the substituents at 2 position) whereas the third describes the stereochemistry of the seven membered ring (orientation of the substituent at 6 position) and it will apply to all perhydroazulene systems under discussion.

The c*is-trans-cis* stereomer with a steric energy of 19.00 kcal/mol (Figure **c**) was found to be the most stable for the *cis*-fused systems from the theoretically possible three other isomers shown in figures **a**, **b** and **d**. Experimental evidences (isolated compounds) showed the formation of *cis*-fused and *trans*-fused systems in 4/1 ratio respectively (indicated by the GC analysis of the mixture) and as can be seen from the X-ray structures of the *cis*-fused systems (Figures 8 / 9 / 12), experimentally, the *cis-trans-trans* stereochemistry for the *cis*-fused system is the most stable one (like in Figure **b**). As the difference between the energies of the theoretically most stable and experimentally most stable isomers is only 0.39 kcal/mol, the experimental findings are nearly in accordance with the theoretical calculation in case of the *cis*-fused system.

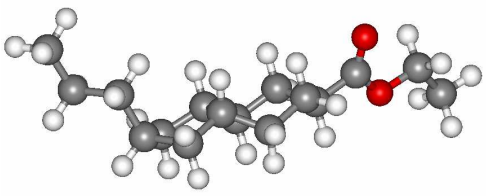


Figure a. *cis-cis-cis* system (20.73 kcal/mol).

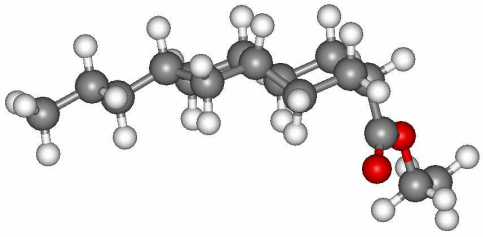


Figure b. *cis-trans-trans* system (19.39 kcal/mol).

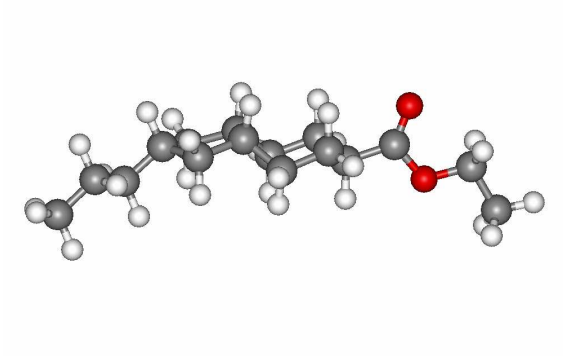


Figure c. *cis-trans-cis* system (19.00 kcal/mol).

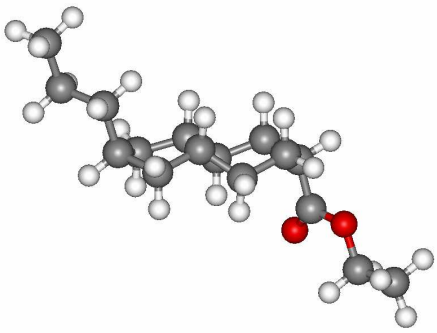


Figure d. *cis-cis-trans* system (21.14 kcal/mol).

For the *trans*-fused systems, the theoretical calculations indicated the stability for *trans-cis-trans* stereomer (Figure **g**) with 20.1 kcal/mol of energy as compared with the three other theoretically possible stereoisomers. The difference of steric energies in the order of 1.1 kcal/mol between the theoretically most stable *cis*-fused system (Figure **c**) and the *trans*-fused system (Figure **g**) shows the stability of *cis*-fused system over *trans*-fused which in turn was confirmed experimentally by the formation of 4/1 ratio of *cis*/*trans* isomers mixture.

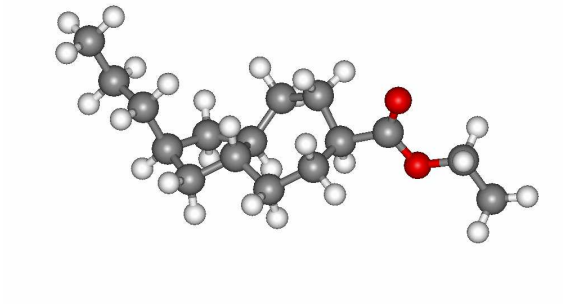


Figure e. *trans-cis-cis* system (21.77 kcal/mol).

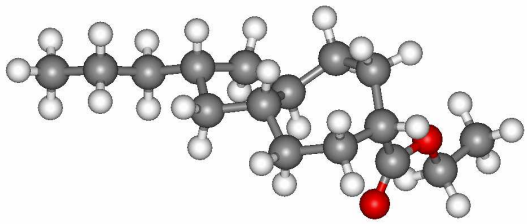


Figure f. *trans-trans-trans* system (20.5 kcal/mol).

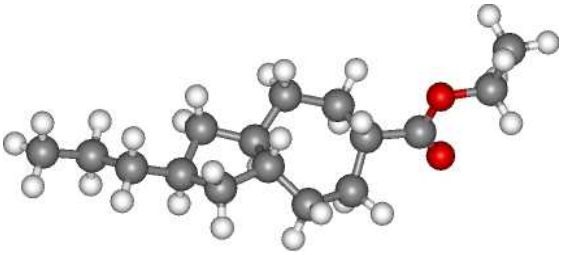


Figure g. *trans-cis-trans* system (20.1 kcal/mol).

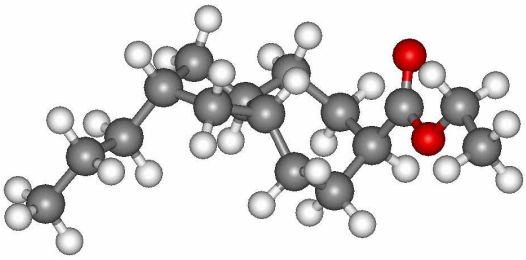
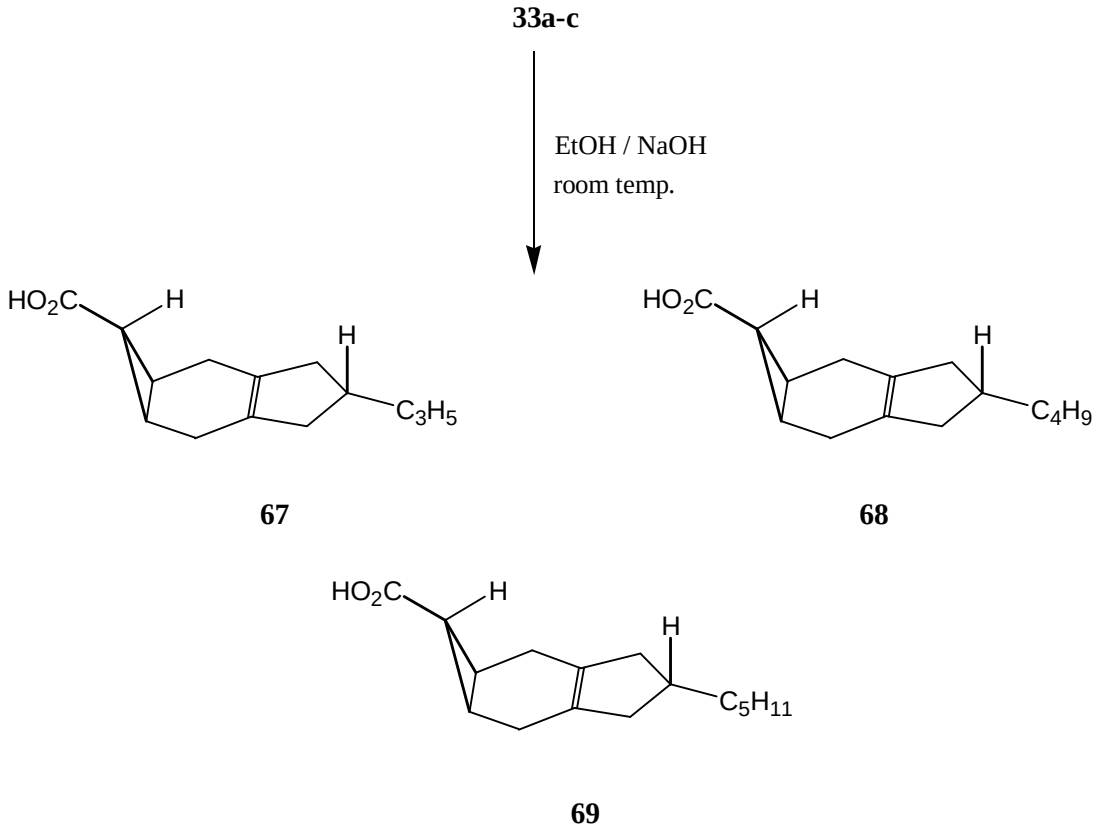


Figure h. *trans-trans-cis* system (22.13 kcal/mol).

2.1.5.3. Stereochemistry of various cyclopropane carboxylic acids

In order to investigate the exact stereochemistry of the various esters, their hydrolysis[58] was carried out in ethanol in the presence of sodium hydroxide; the resulting acids were recrystallized from hexane and dichloromethane to prepare single crystals suitable for X-ray studies. All of the acids obtained were characterized by their usual spectroscopic and analytical data which are given separately in the experimental section.



67 **68**

69

Scheme 22. Hydrolysis of the esters **33a-c**

As shown in figures 1-3, the cyclohexene rings in each of the three compounds are only slightly twisted by 0.1(2)° to 18.1(4)°. The cyclopropyl groups are strongly folded to their neighbouring planes of the six membered rings by 72.4(1)° to 72.7(1)°. The carboxyl groups are all in the *exo*-position with a bisecting orientation of the carbonyl group to the three-membered ring 89.5(1)° and 88.9(1)° in compound **68** and have nearly bisecting arrangements in **69** (85.2(1)° and 85.5(1)°). As a reason of this nearly optimal orbital overlap, relatively long vicinal bonds from 1.51 to 1.53Å and short distal bonds from 1.48 to 1.49Å in the cyclopropyl subunits were found. The carboxylic groups build dimeric pairs in the crystal packing (see Figure 4) by hydrogen bonding. Disorder effects were found at the envelope form of the five-membered rings in **68** and one of both isomers of **69**. Referring to

this ‘tops’ of the envelope-shaped cyclopentene subunits point in complementary directions (Figures 1, 2 and 3 show only one of the disordered positions).

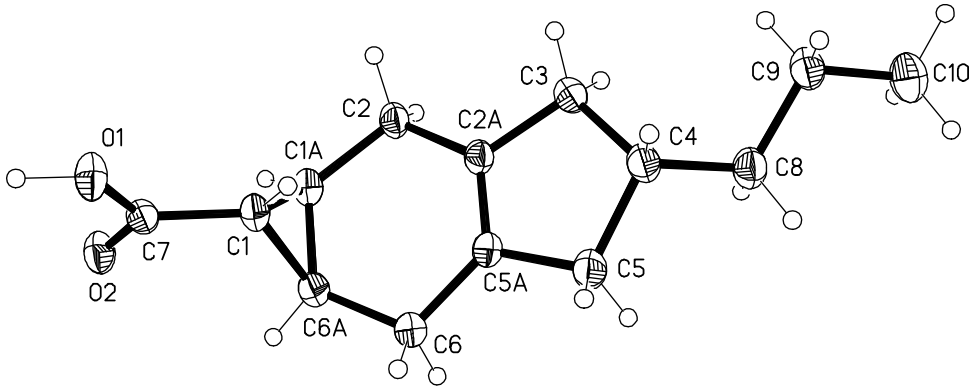


Figure 1. Structure of **67** in the crystal

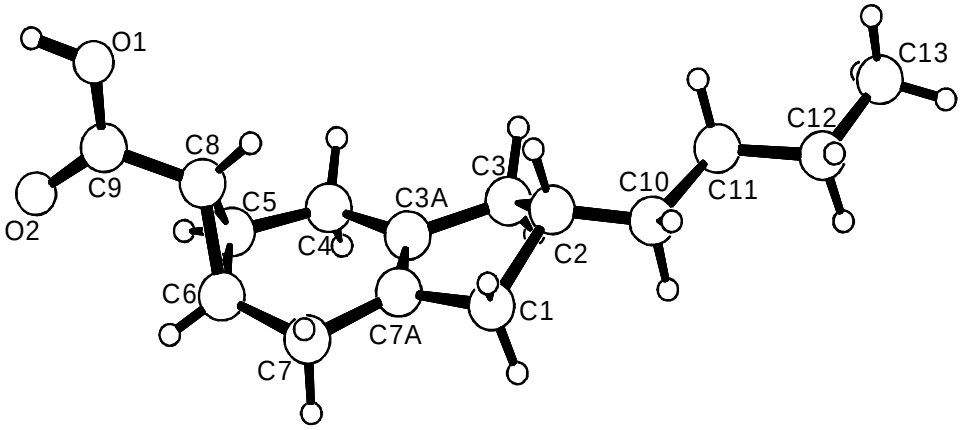


Figure 2. Structure of **68** in the crystal. It is shown only one of the disordered positions of C2, C11, C12 and C13.

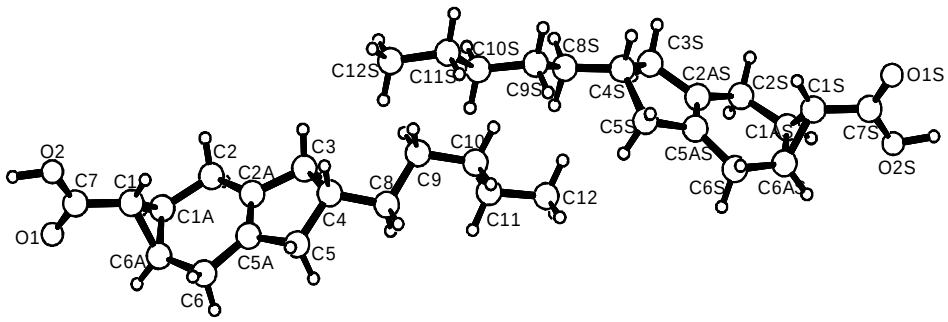


Figure 3. Structure of **69** in the crystal. It is shown only one of the disordered positions.

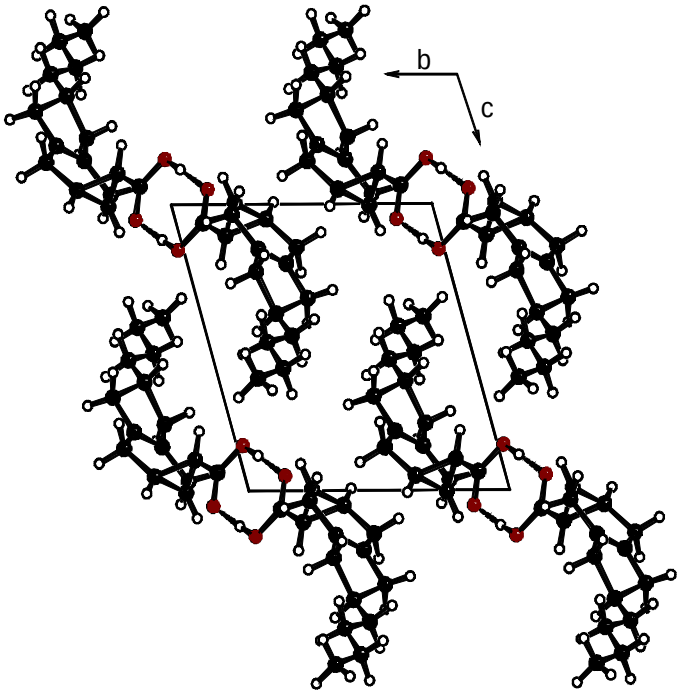
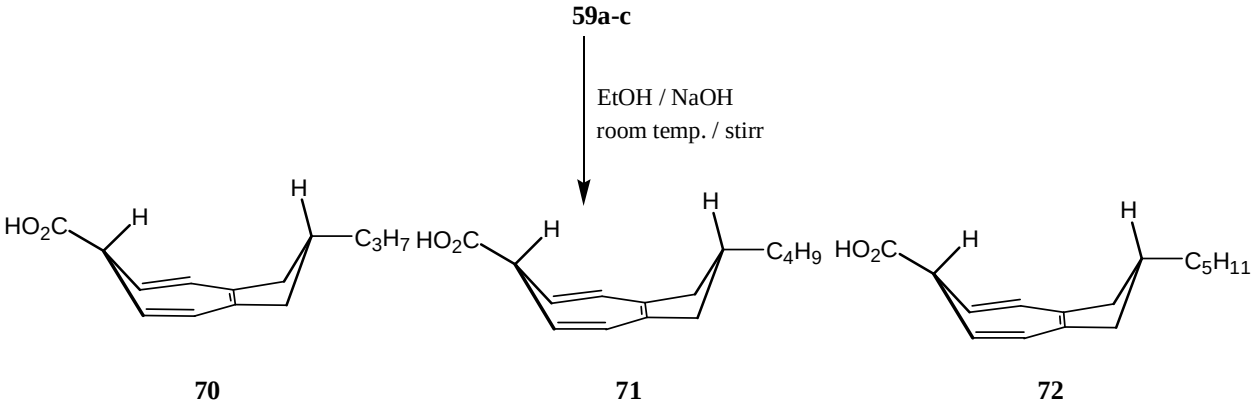


Figure 4. Packing diagram of **68**; view along the crystallographic a-axis. Hydrogen bonds are shown as fragmented lines.

In summary, these results show that the carbene has added to the outer double bond of **56a-c** ‘‘away’’ from the alkyl group (*trans*) and with the ester/acid function pointing to the outside (*exo*) of the molecule. Both arrangements are in accordance with expectations.

In order to confirm the structures of various partially hydrogenated azulene derivatives **59a-c**, their hydrolysis was carried out in ethanol/sodium hydroxide mixture yielding acids **70**, **71** and **72** which were recrystallized from hexane/dichloromethane mixture to get single crystals for **70** and **72** for X-ray analysis while compound **71** could not be recrystallized. All of these derivatives were also characterized by their spectroscopic and analytical data and from the similarity of these data we assume that **71** has similar stereochemistry as **70** and **72** as shown in Scheme 23.



Scheme 23. Hydrolysis of esters **59a-c**

Due to the partial hydrogenation of the azulene skeleton in compounds **70** and **72,** the cycloheptatriene subunits were found in a boat shape conformation. The interplanar angles between the calculated planes C5/C6/C7 to C4/C5/C7/C8 are 55.5(1)° and 52.1(7)°, the corresponding angles between C4/C3A/C8A/C8 to C4/C5/C7/C8 are 28.6(1)° and 28.5(1)° for **70** and **72**, respectively. A slight envelope-conformation was noticed in the five-membered ring of **70** with 21.7(2)° between C1/C2/C3 and C1/C3/C3A/C8A. The analogous hydroazulene derivative **72** is not discussed in this context because C2 was found at two positions, each with 50 % multiplicity. As can be seen in the packing arrangement of **70** in Figure 6, pairs of two molecules are linked together via hydrogen bonds across a center of symmetry. Similar dimeric connections were found in the packing arrangement of **72.**

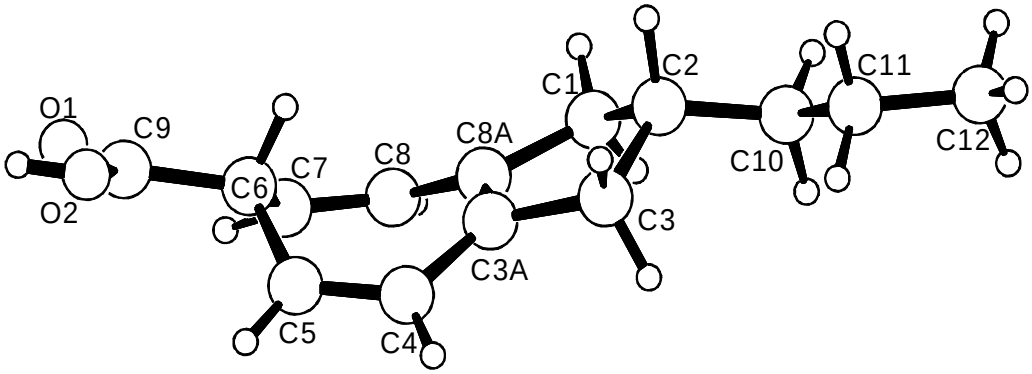


Figure 5. Structure of **70** in crystal and its packing diagram; view along the crystallographic b-axis.

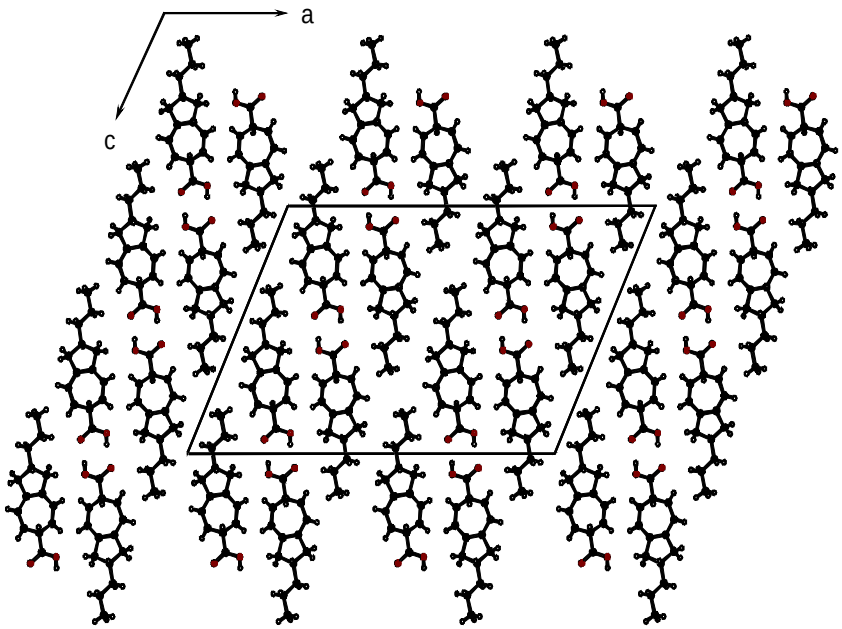


Figure 6. Packing diagram of **70**; view along the crystallographic b-axis.

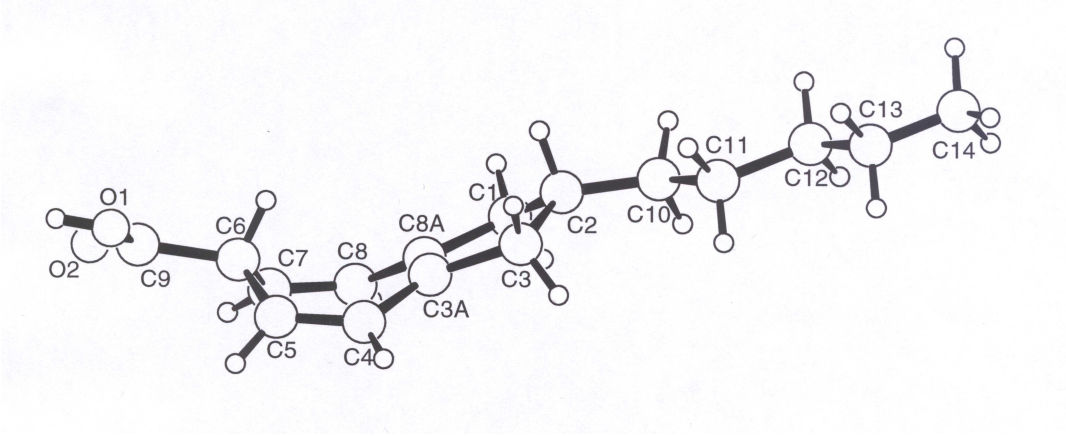
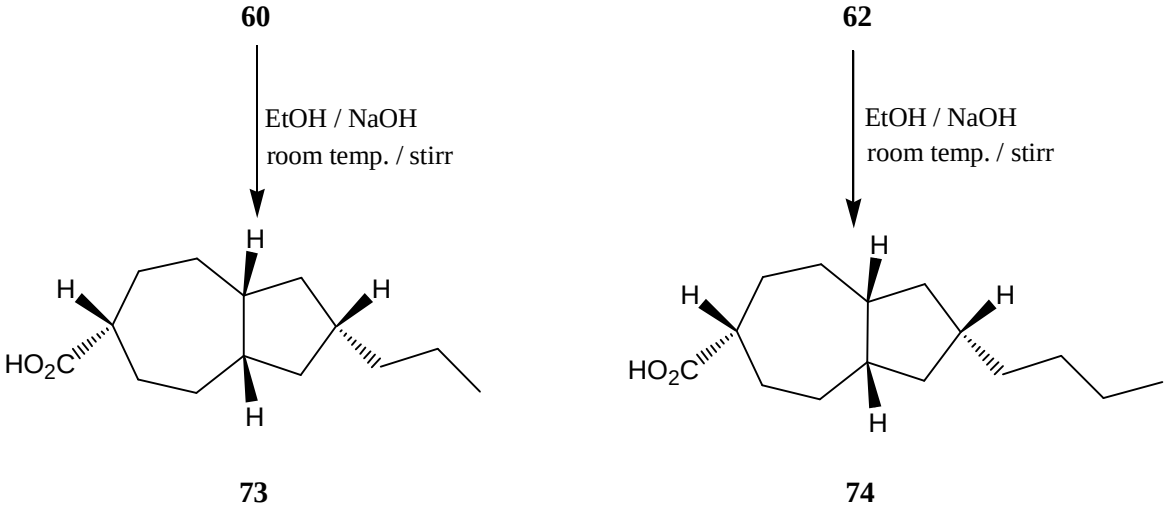


Figure 7. Structure of **72** in crystal; only one of the both disordered positions of C2 is shown.

In principle the double bonds in the seven-membered of these derivatives could be arranged in different order, the various isomers being connected by symmetry-allowed 1,7-hydrogen shifts. That only the shown isomers are generated, it probably has to do with their greater thermodynamic stability, as with a double bond at the ring junction an isomer results with the most highly substituted double bond possible.

Finally our interest was to investigate the *cis*-fused isomers of the perhydroazulenes which lead us to hydrolyse the esters **60** and **62** by employing the same procedure as mentioned before to get acids **73** and **74** in the form of colourless solids which on recrystallization from hexane/dichloromethane yielded suitable crystals for X-ray analysis. X-ray data showed that in both the acids, protons at ring junction are pointing in the same direction giving rise to *cis*-

fused systems as required. The cycloheptane ring was found twisted and due to hydrogen bonding between the acids, dimeric forms are produced as can be seen in Figure 9. The complete spectroscopic and analytical data of acids **73** and **74** can be found separately in the experimental section.



Scheme 24. Hydrolysis of perhydroazulene systems **60/62**

With these experiments the stereostructures of our most important intermediate rest on solid grounds.

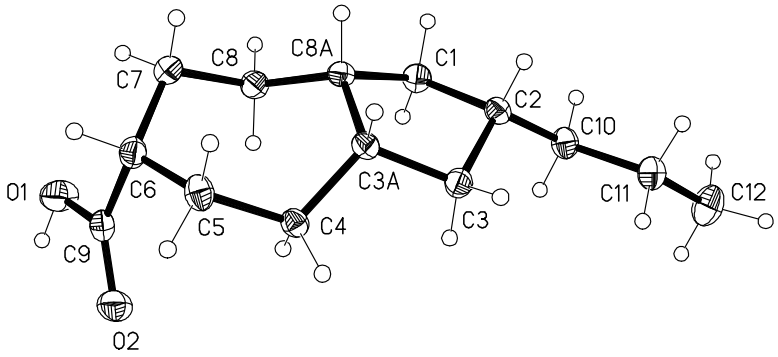


Figure 8. Structure of **73** in the crystal

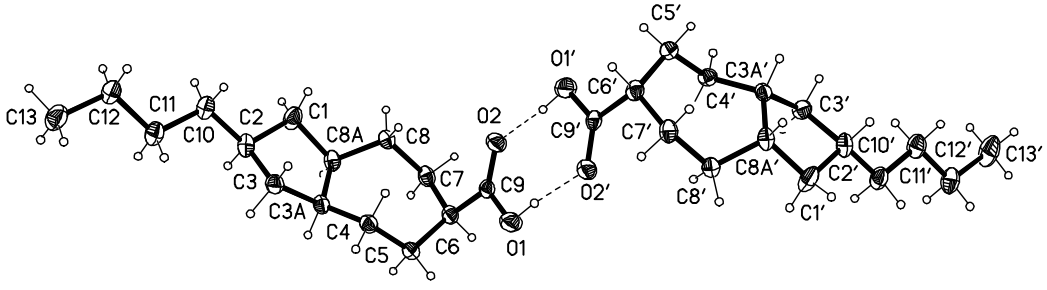
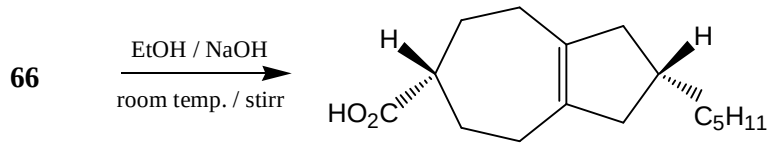


Figure 9. Structure of **74** in the crystal

In order to confirm the stereochemistry of **66**, it was hydrolyzed in the same manner as the derivatives above to obtain acid **75**. However, the acid obtained could not be recrystallized to provide single crystals suitable for X-ray analysis. However, disappearance of a quartet at 4.14 ppm as well as one triplet at 60.09 ppm in the ^{1}H and ^{13}C spectra, respectively, due to the methylene protons of the ester group, indicated the formation of **75**. Complete spectroscopic and analytical data of acid **75** can be found separately in the experimental section.

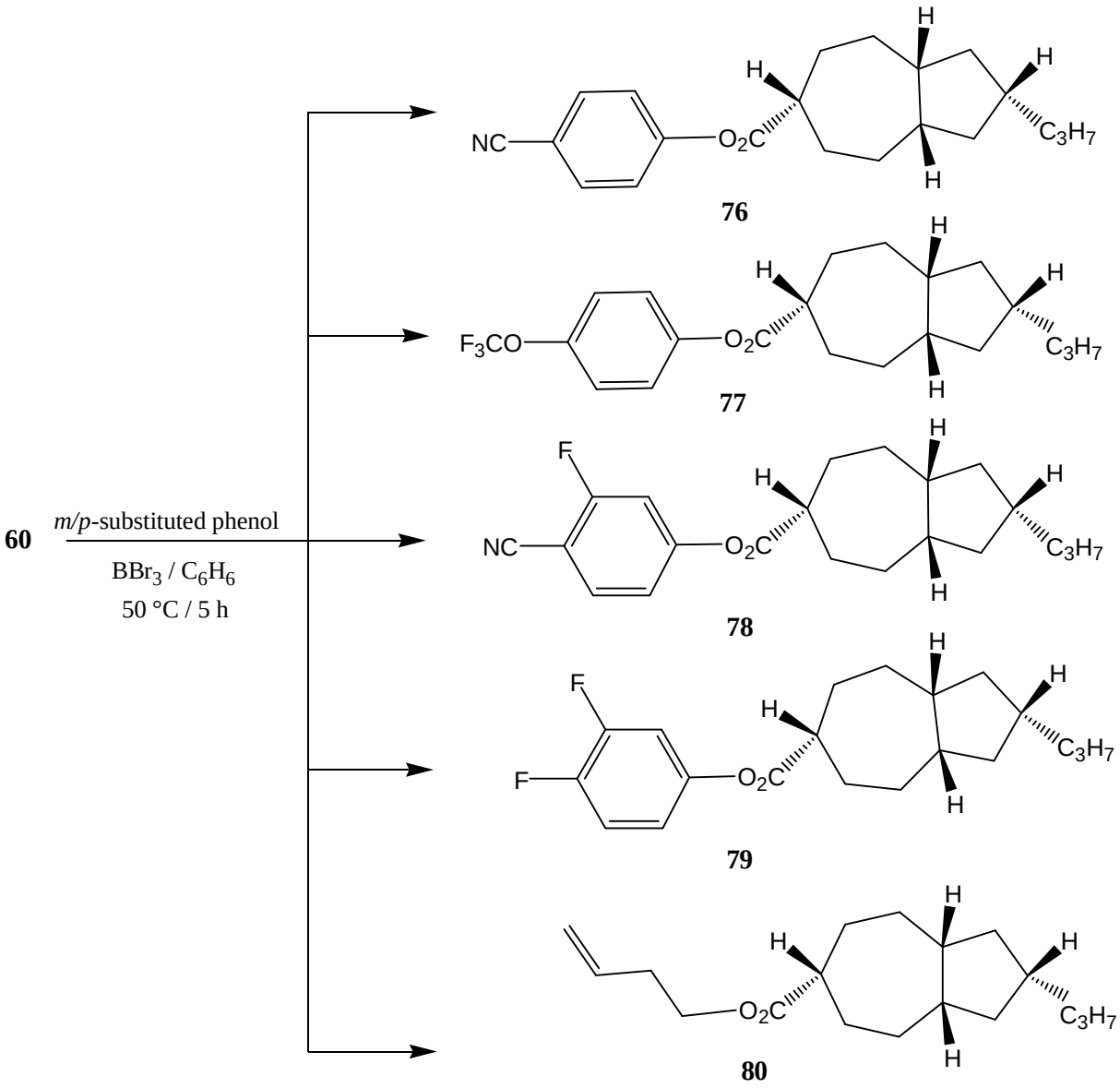


75

Scheme 25. Hydrolysis of ester **66**

2.2. Transesterification of *cis*/*trans*-fused perhydroazulenes

Materials with rod like structures are important candidates for mesogenic properties. Perhydroazulenes with *cis*-fused systems were employed to synthesise these materials for exploratory investigations. One way, of course, to extend the length of the above compound is to attach a moiety at the ester side of the molecule and the simplest way is given by the attachment of *para*-substituted phenols. Since saponifying perhydroazulene esters to acids followed by formation of the acid chloride and then esterification constitutes a multi-step sequence, we decided to use transesterification for the preparation of these materials. There are many procedures[59] for transesterification employing various reagents. The method of Yazawa et al.[60] was used here for the transesterification of **60** by using boron tribromide in benzene and subsequent reaction with various *p*-substituted phenols. The addition of excess amounts of phenols resulted in short reaction times with excellent yield of the new ester (65 %). Compounds **76-80** were synthesised for the initial investigation of the textural features. It is important to note that the non-polar end in all these materials is the same i.e. a propyl chain while a different substitution pattern was generated at the other terminus of the molecule. Various polar groups were selected like CN, F, OCF_3 etc for this purpose in order to synthesise model materials for the study of the structure-property relationships.

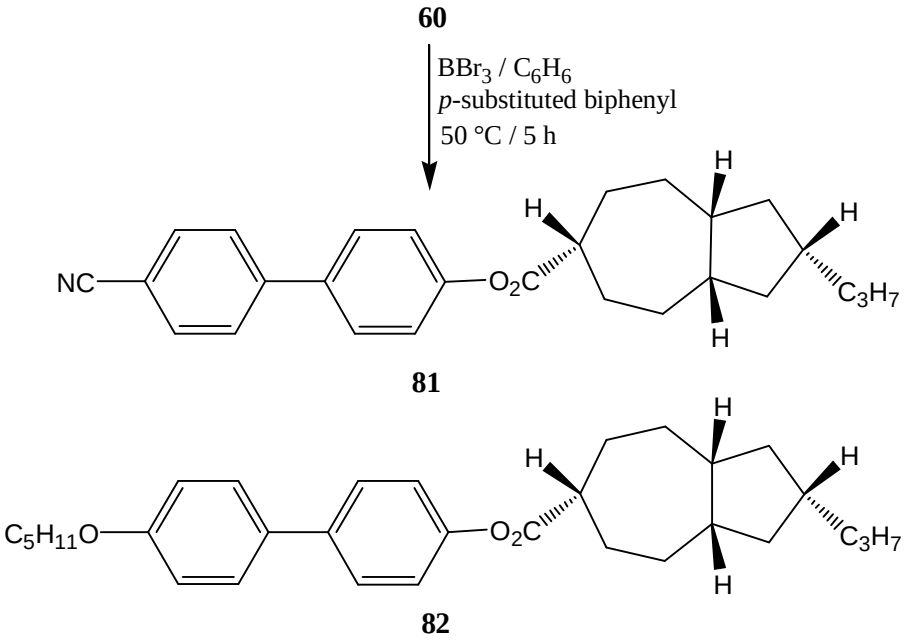


Scheme 26. Formation of the derivatives **76-80**

All of the above materials except **76** were obtained either in the form of semisolid or liquid substances. Compound **76** was obtained in the form of a colourless solid which was recrystallized from hexane and dichloromethane to get single crystals for X-ray analysis. However, the structure of **76** could not be resolved from its X-ray data. The stereochemistry in case of **76-80** at position 2 and 6 as well as in the ring junction is supposed to be the same as discussed earlier for **60**. All of the above compounds were characterized by their usual spectroscopic and analytical data which are given separately in the experimental section.

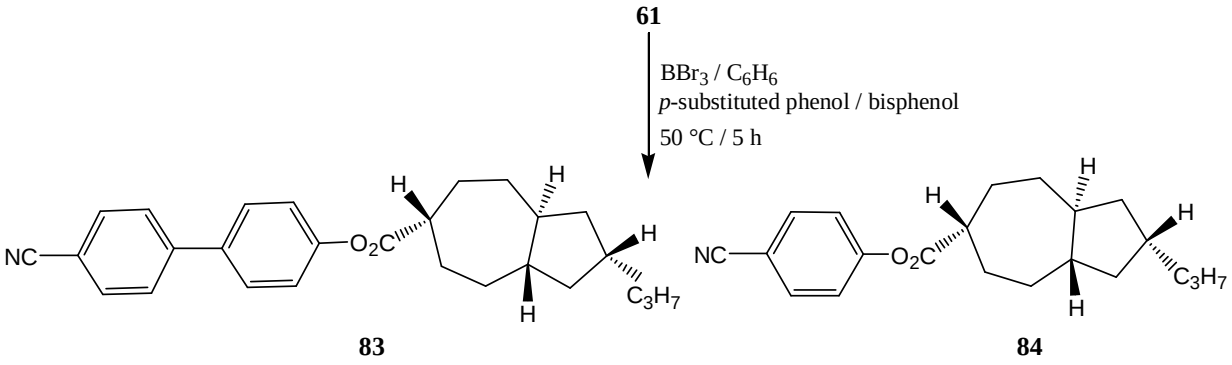
In order to increase the length of the new materials based on perhydroazulene ring systems, biphenyl derivatives like **81** and **82** were also prepared from the ester **60** by transesterification as discussed earlier. The stereochemistry in case of **81** and **82** is supposed

to be the same, *cis-trans-trans*, as described earlier for **60**. All of these compounds are fully characterized by their usual spectroscopic and analytical data given separately in the experimental section.



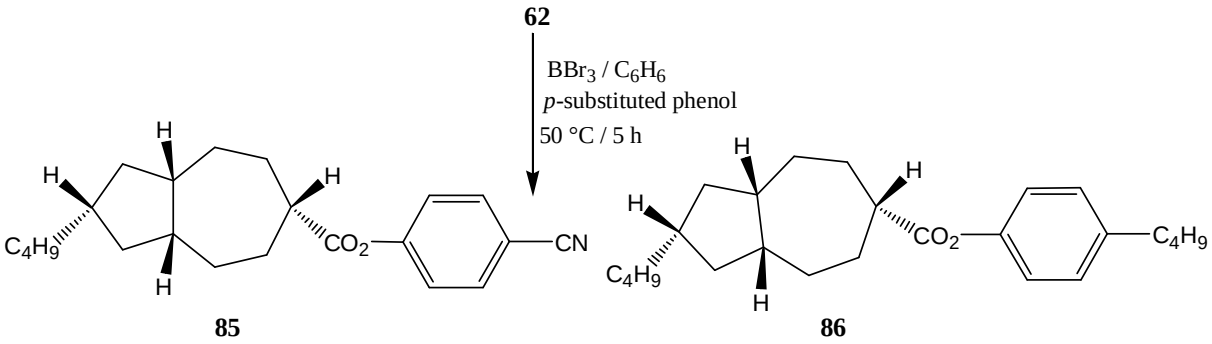
Scheme 27. Synthesis of biphenyl derivatives **81 / 82**

The *trans*-fused ester **61** was also transesterified in the same way and provided **83** and **84** for further studies. It was possible to recrystallize **84** to get pure crystals, however, due to deformed nature, the structure of **84** could not be resolved. The stereochemistry of **83** and **84** at the ring junction and at both terminis (2 and 6) is supposed to be the same (*trans-trans-trans*) as discussed earlier for **61**. Both of these compounds were fully characterized by their usual spectroscopic and analytical data given separately in the experimental section.



Scheme 28. Synthesis of *trans*-fused derivatives **83 / 84** of perhydroazulene

As terminal groups play a crucial role in determining the properties of new LC materials, non-polar terminal groups were changed as in **62** where the butyl group was used instead of propyl. Transesterification of **62** resulted in **85** where the polar end group is cyano and **86** where both terminal groups are non-polar. Compound **85** was obtained as a colourless solid which was recrystallized from hexane/dichloromethane to provide pure crystals of X-ray quality, while compound **86** was obtained as a yellowish solid which could not be recrystallized. The X-ray structure of **85** (Figure 10) shows the *cis-trans-trans* geometry of the system which is the same pattern as shown for MM3 calculations for such systems (Figure **b**, 2.1.5.2). Both of these compounds were further characterized by their usual spectroscopic and analytical data given separately in the experimental section.



Scheme 29. Synthesis of **85 / 86**

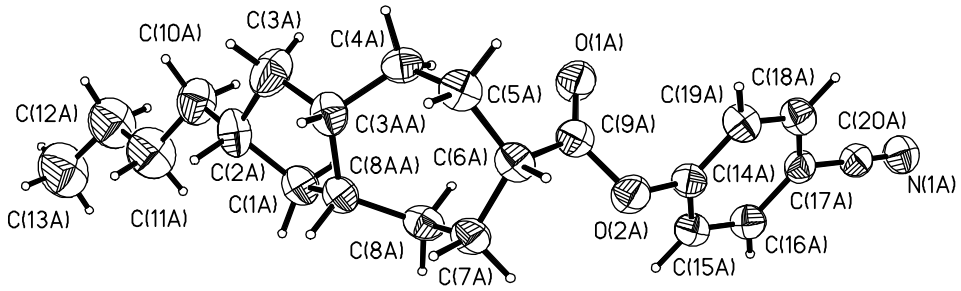
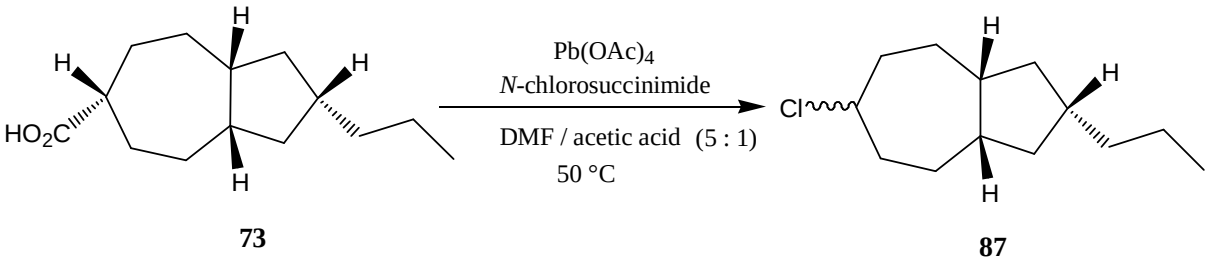


Figure 10. Structure of **85** in the crystal

2.3. Modified Hunsdiecker degradation of 73 for the synthesis of 87

Compound **87** was considered to be an important intermediate for Friedel-Crafts reactions to establish a direct connection of the perhydroazulene system with a variety of *p*-substituted aromatic systems. From the various routes for such conversions, the Hunsdiecker reaction was found to be the most appropriate. There are various modification of the classical Hunsdiecker process[61] such as the decarboxylation of carboxylic acids with lead tetra-

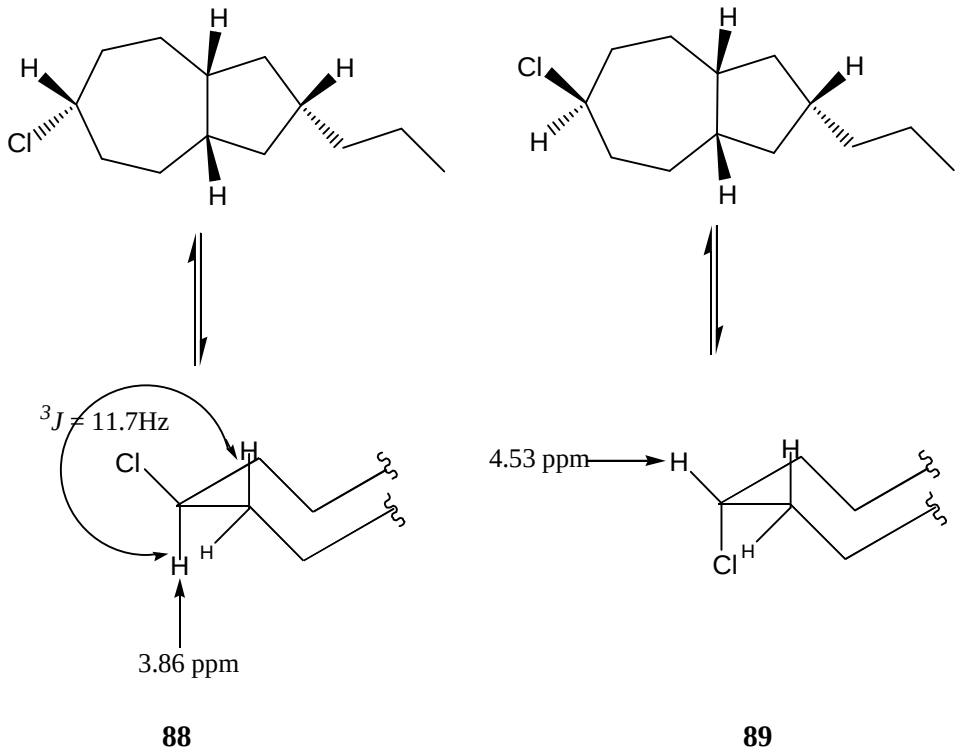
acetate and lithium chloride in refluxing benzene;[62] however, all these protocols have one or the other drawback. We selected the halodecarboxylation method of Becker et al.[63] for our system in which a 5:1 mixture of dimethylformamide and glacial acetic acid was used as the solvent and *N*-chlorosuccinimide as the chlorine donor. At 50 °C the chloride **87** was obtained in 68 % yield from acid **73**.



73 **87**

Scheme 30. Synthesis of **87**

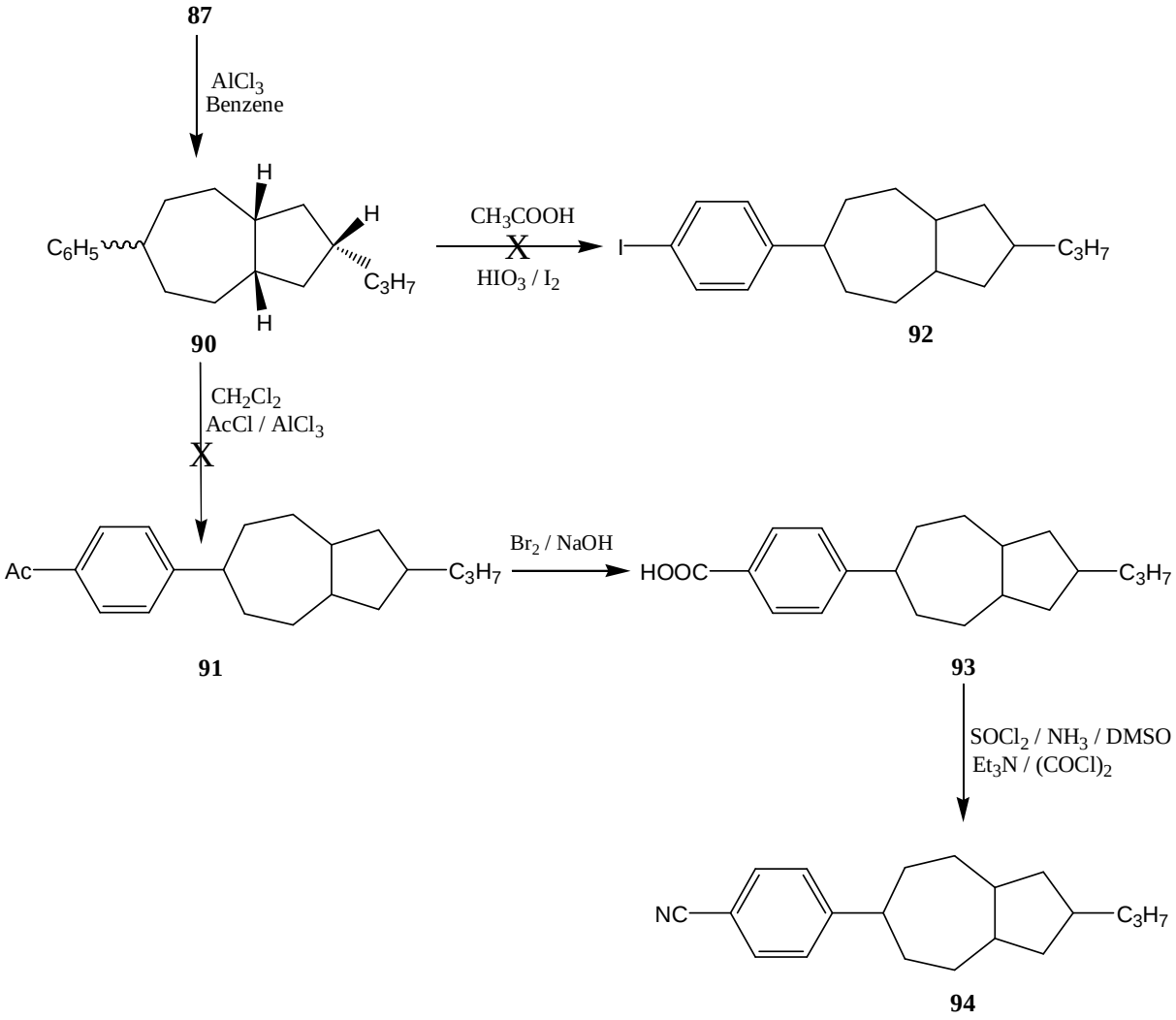
Starting from the pure *cis*-fused system **73** we were able to get a mixture of two isomers of **87**, the chorides **88** and **89**, with overlapping signals in the GC due to the same polarity and molecular mass. However, in the NMR spectra it was possible to differentiate between the two isomers. The presence of the two one-proton multiplets at δ = 4.53 and 3.86 (integral ratio 1:1) indicated the sample to be a mixture of stereoisomers. The signal at δ = 3.86 is a triplet of triplet with coupling constants of 11.7 Hz and 4.1 Hz. The larger coupling indicates an axial orientation of this proton, i.e. an equatorial orientation of the chlorine substituent (**88**). The signal at δ = 4.53 is not well resolved but is of much narrower width than the one at δ = 3.86, hence, no larger axial-axial coupling is taking place and the proton should be in a more or less equatorial orientation resulting in turn in a preferentially axial chlorine substituent (**89**). From the integrals of these protons it is concluded that **88** and **89** are produced in 1/1-ratio.



88 **89**

Scheme 31. Some stereochemical aspects of the chloride **87**

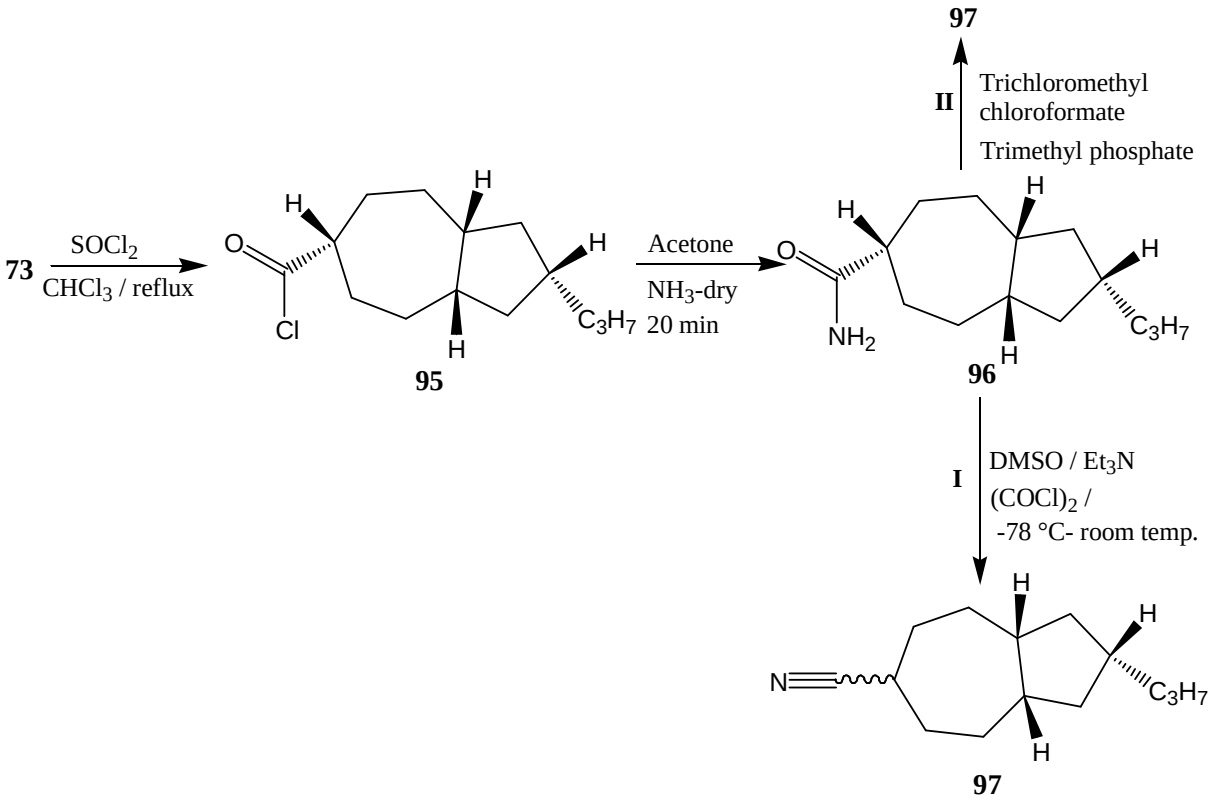
Continuing the synthesis, **87** was subjected to a Friedel-Crafts reaction[64] in the presence of benzene and aluminium chloride. Hydrocarbon **90** was produced as colourless oil in quite good yield (0.6 g, 62 %). It was thought to continue the synthetic route, outlined in scheme 32, for the synthesis of compound **94** which was supposed to have some mesogenic properties. Iodination[65] at the *para*-position of **90** to get **92** failed. Various iodination methods were used, but in all cases mixtures of products were collected and the desired **92** was not isolated. After repeated failure to reach **94** by iodination (which we wished to convert to the corresponding nitrile),[66] the synthetic route was changed and another approach was employed. Friedel-Crafts acylation with acetylchloride, should lead to **91** which was considered to be an intermediate to reach **94** via **93**. But after many attempts, compound **91** could not be obtained in pure form from a highly complex product mixture. So these experiments were not pursued further at present.



Scheme 32. Possible synthetic route to **94**

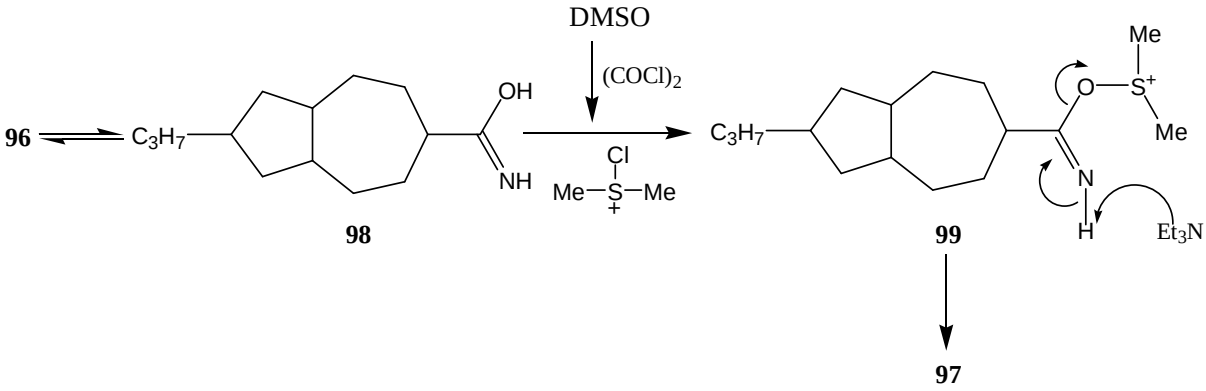
2.4. Synthesis of the nitrile derivative 97

After the failure to get **94** with *p*-cyanophenyl as the terminal group in the basic core of the perhydroazulene system, further attempts focused on synthetic materials with the CN group directly attached to the core structure of the perhydroazulene system. Therefore, the route leading towards the synthesis of nitrile **97** started from the *cis*-fused acid **73**, which was obtained by hydrolysis of ester **60**. The acid chloride **95** obtained[67] was treated with dry NH_3 in acetone to get the amide (0.2 g, 40 %) **96** which was characterized by its usual spectroscopic and analytical data given separately in the experimental section.



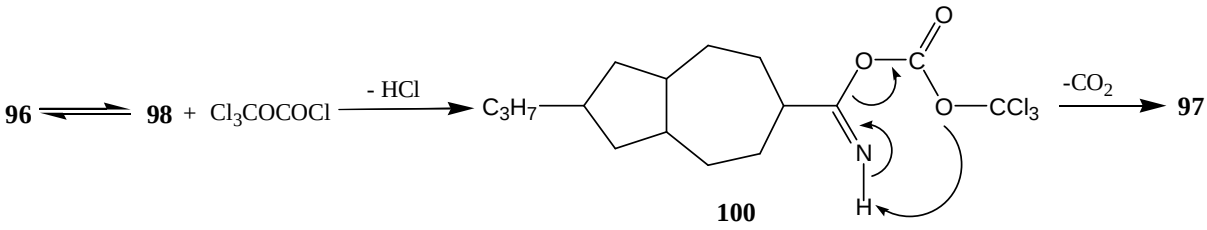
Scheme 33. Synthesis of the nitrile **97**

Although **96** was almost pure with a sharp melting point, the NMR spectrum showed traces of impurities which could not be separated fully by column chromatography due to the polar amide group. The derivative was therefore subjected to dehydration in the next step. For conversion of **96** to **97** first the method of Nakajima et al.[68] (**I**) was considered in which Swern oxidation conditions, $(COCl)_2$-DMSO and Et_3N as dehydrating agent, were employed to obtain the desired **97**. By this method nitrile preparation was achieved by successively adding $(COCl)_2$ and Et_3N to a mixture of **96** and DMSO in CH_2Cl_2 at -78 °C, which was then warmed to room temperature. However, the yield was quite low in this case (10 mg, 22 %). A plausible mechanism for the dehydration is shown below (Scheme 34). First the amide **96** rearranges to **98**, which is then activated by DMSO to provide the intermediate **99** which by a concerted mechanism fragments to the nitrile **97**.



Scheme 34. Mechanistic route to **97** under Swern oxidation conditions (**I**)

The procedure of Mai et al.[69] (**II**) was used to overcome the problem of low yield in the previous method. By this route a simple dehydration of carboxamide **96** to **97** using the liquid 'diphosgene', trichloromethyl chloroformate, was achieved in moderate yield (20 mg, 43 %). The short reaction time, simple work-up, moderate yield and mild reaction conditions demonstrated the usefulness and versatility of this method. A plausible mechanism (Scheme 35) shows the formation of intermediate **100** which by a concerted mechanism is converted to **97**.



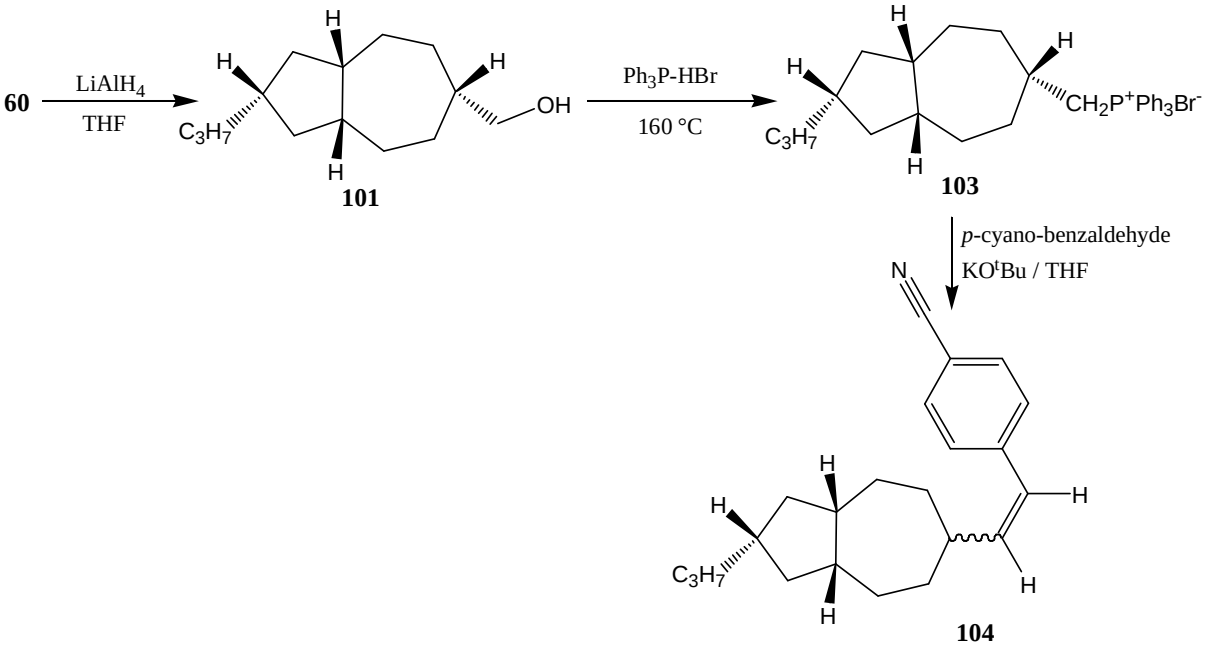
Scheme 35. Mechanistic route to **97** with diphosgene (**II**).

Derivative **97** was obtained in the form of a mixture of isomers which could not be separated due to almost the same polarity (R_F = 0.70/0.75). It is important to note that starting from pure acid **73**, a mixture of isomers of **97** was obtained which might be due to the axial and equatorial hydroxyl substituents at position 6 of the perhydroazulene system resulting in equatorial or axial CN group in the same manner as described earlier in Scheme 31 for the chloride derivative **87**.

2.5. Synthesis of 104 by Wittig reaction

In order to extend the length of perhydroazulene system, compound **104** was synthesised, expected to possess novel textural features of mesogenic materials. To obtain alcohol **101**, ester **60** was subjected to reduction with $LiAlH_4$ in THF. Although the yield was only moderate (0.5 g, 67 %), it was good enough to proceed further. Having prepared pure alcohol

101, the next step constituted a Wittig coupling to get **104**. To avoid the formation of halide,[70] the method of Hamanaka et al.[71] was employed where the phosphonium salt **103** was prepared directly from the alcohol in the presence of commercially available triphenylphosphonium hydrobromide. Intermediate **103** was not isolated and characterized but directly coupled with *p*-cyano-benzaldehyde in the presence of potassium tertiary butoxide in THF.



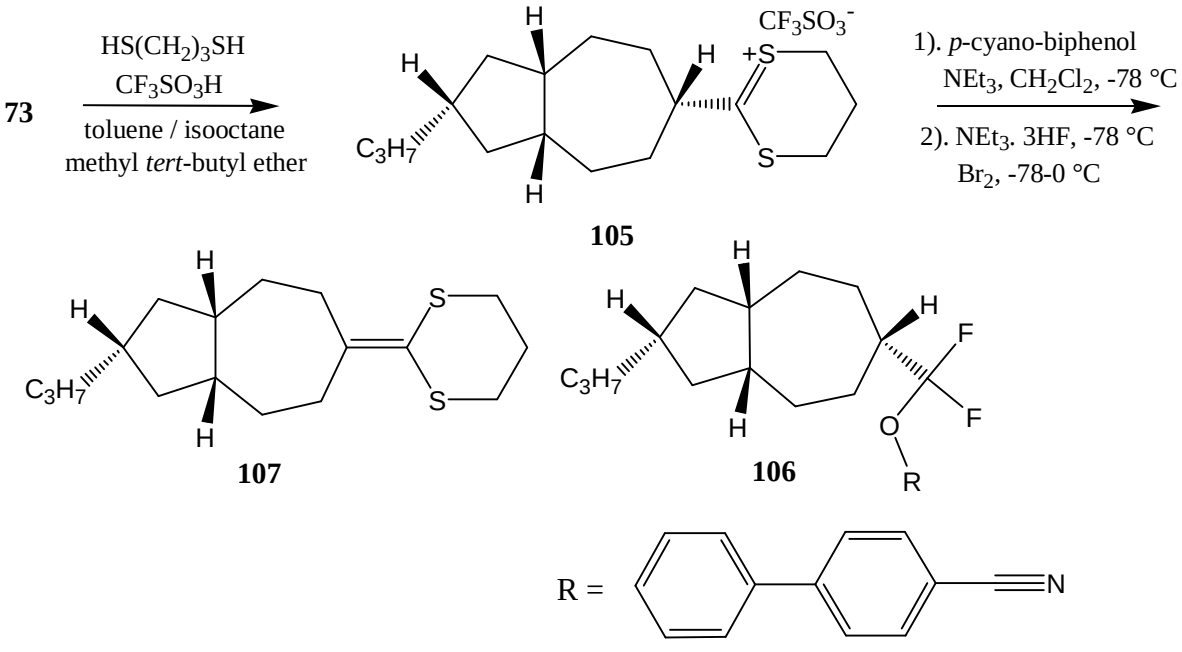
Scheme 36. Synthetic route to **104**

The obtained derivative **104** is supposed to be a novel candidate for a mesogenic compound since it gives the opportunity to various novel derivatives by hydrogenation of the double bond, its 1, 2-difluorination etc. For **104** the *cis* coupling constant of 11.7 Hz for the olefinic double bond was of particular diagnostic value. Although all the analytical data are consistent with the proposed structure, the ^{1}H NMR spectrum clearly indicated the presence of other isomers also with *cis* coupling constant of 11.7 Hz for the olefinic double bond. The exact stereochemistry of the other isomer remains to be established; however, it might have the same orientation of 6-H as mentioned earlier for **87** in scheme 31.

2.6. Towards the synthesis of difluoromethylene-bridged materials

It was supposed that the insertion of a difluoromethylene bridge into a specific location of the core structure of a perhydroazulene system would result in a class of materials that would exhibit a pronounced improvement of essentially all mesogenic properties.

Although a variety of methods are known for the preparation of aryl α,α-difluorobenzyl ethers,[72] the efficient synthesis of aryl and alkyl α,α-difluoroalkyl ethers was an unsolved problem until Kirsch et al.[13] reported the insertion of the difluoromethylene bridge into the basic phenyl-bicyclohexyl structure. Employing the same synthetic strategy as described in the literature, dithianylium triflate **105** was prepared from the acid **73** in the presence of 1,3-propanedithiol, trifluoromethylsulfonic acid, toluene, isooctane and methyl *tert*-butyl ether. Conversion of **105** to **106** under the conditions shown in scheme 37, resulted in exclusive formation of ketenedithioketal **107** while some traces of **106** were formed indicated by GC-MS spectrum. The treatment of the dithianylium salt **105** with base (triethyl amine) resulted in quantitative deprotonation of the cation to the ketenedithioketal **107**. It has been reported that conducting the whole reaction sequence (formation of the dithioorthoester of **105**, subsequent halonium-mediated fluorodesulfuration (triethylamine tris(hydrofluoride), bromine) as a one-pot procedure at -78 °C should furnish the desired product **106**, but various attempts lead to **107** while **106** could not be isolated. Compound **106** could not be characterized fully due to the lack of material while **107** was characterized by its usual spectroscopic and analytical data given separately in the experimental section.

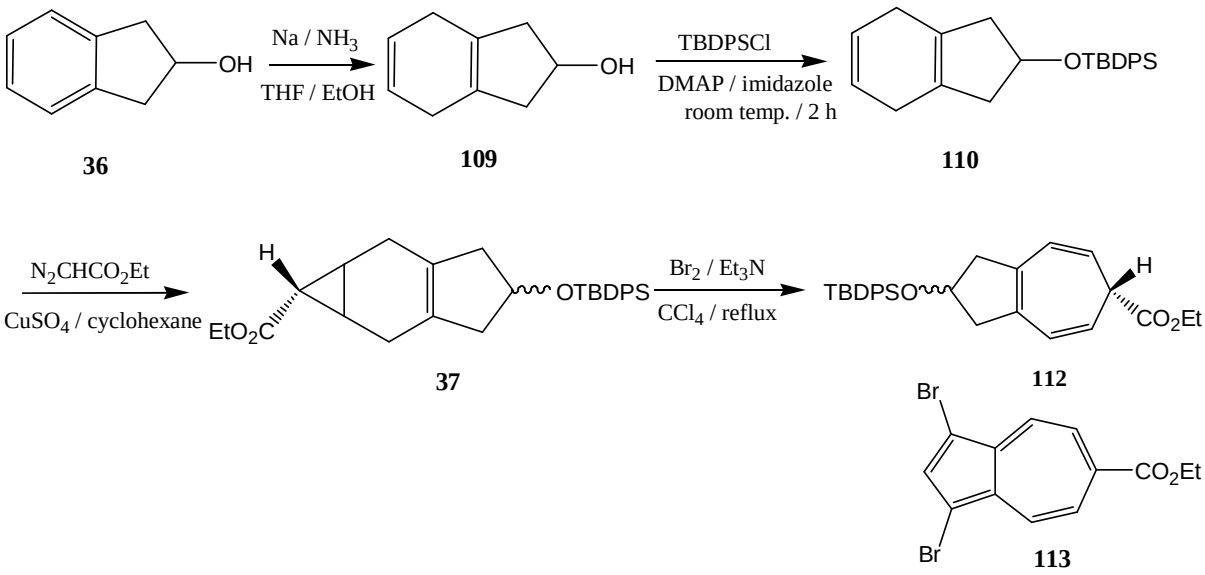


Scheme 37. Synthetic route to the biphenyl nitrile **106**

2.7. Synthesis of propyl 1, 3-dibromoazulene-6-carboxylate 113

It is clear from the ongoing discussion that derivatization at position 6 is easy while any change at position 2 of the system would require the repetition of the whole synthesis. So in

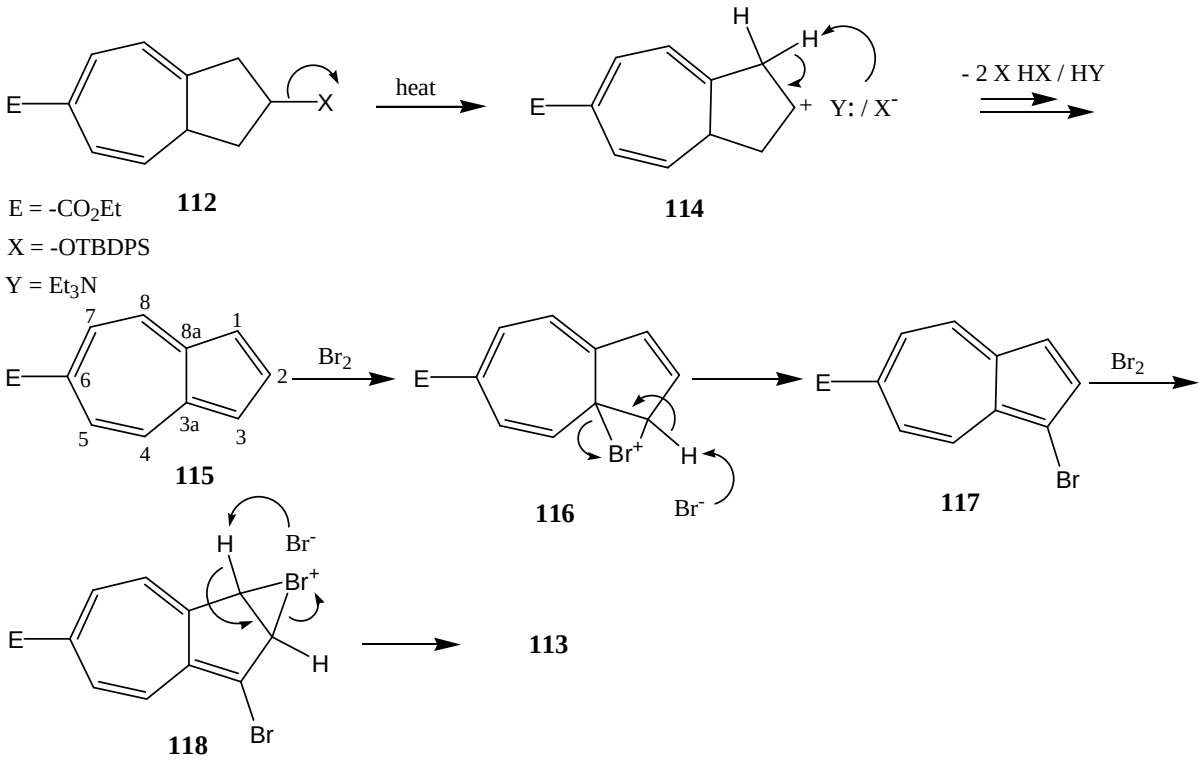
order to get a perhydroazulene system with the possibility of derivatisable or replaceable group like OH or any halogen at position 2 new synthetic route outlined in scheme 38 was developed. This new strategy resulted in compounds like **112** which is a potential intermediate for a large variety of new materials, and **113** which is a new azulene derivative formed during the course of the reaction. Starting from inexpensive and readily available 2-indanol **36** it was possible to prepare 4,7-dihydro-2-indanol **109** by Birch reduction in almost quantitative yield. The hydroxy function of **36** was protected by tertiary butyl diphenyl silyl chloride in the presence of dimethyl amino pyridine and imidazole[73] at room temperature, also in quantitative yield. The protection of the hydroxy function was carried out to direct the carbene addition to the external double bond in the next step. The protected 4,7-dihydro-2-indanol **110** was subjected to carbene addition in the presence of ethyldiazoacetate and dried copper sulfate in dried cyclohexane to yield the carbene adduct **37** in 75 % yield while some of the diethyl fumerate which was formed during the reaction was also isolated as well as some unreacted starting material. The yield in this reaction was improved by increasing the carbene addition time and using thoroughly dried copper sulfate and cyclohexane as the solvent. Ring expansion of compound **37** was performed in the presence of bromine and triethyl amine with carbon tetrachloride as solvent. In this reaction bromine was added first to the double bond and later removed as a hydrobromide salt by adding triethylamine and refluxing the mixture for several hours. This resulted in cyclopropane ring opening to provide **112** as the major product in 52 % yield, while **113** as a minor component was produced in 10 % yield. The formation of **112** was expected during the reaction, while **113** formed by rearrangement and bromination of **112**. It is important to note that the yield of **113** can be increased by just prolonging the reflux time which might be due to the rearrangement of **112** which forms first. The new adducts were characterized by the usual spectroscopic data, which are summarized in the experimental section. The stereochemistry at position 1 in case of **37** and position 6 in case of **112** is supposed to be the same as discussed earlier in case of carbene adducts **33a-c** and **59a-c**; however, the stereochemistry at position 4 remains to be established.



Scheme 38. Synthesis of 1,3-dibromo azulene derivative **113** and a 2,6-disubstituted tetrahydroazulene derivative **112**

A plausible mechanism for the formation of **113** could involve the following steps (Scheme 39). On refluxing the mixture for a longer time, the side chain from the rearranged **112** which is too bulky can just be cleaved off leaving behind a secondary carbocation **114** which can be stabilized by a proton abstraction with a negatively charged oxygen atom of the leaving group or triethylamine present in the mixture.

Very likely the driving force of the transformation is the formation of more stable aromatic azulene nucleus. As position 1 and 3 of azulene are more susceptible for electrophilic attack,[44] and the presence of bromine results in the formation of brominated product **113**. First bromine adds to the double bond at 1 and 8a which results in the formation of bromonium **116** while, the bromide ion abstracts a proton resulting the formation of the mono substituted product **117** instead of the addition product thus restoring the aromaticity of the molecule. The abstraction of a proton from **118**, when a second bromine molecule adds at the double bond between position 2 and 3, is more likely to take place from position 3 which is more accessable to bromide; this results in the formation of **113**.



Scheme 39. Mechanism of formation of dibromide **113**

Compound **113** was obtained as a dark blue solid, which was recrystallized from dichloromethane and hexane to yield dark green needles suitable for X-ray analysis. Two crystallographically independent molecules were found in the asymmetric unit. The azulene frameworks of both the molecules were planar with mean deviations of 0.01 and 0.02 Å out of the calculated ring planes. Planes defined by the atoms of the ethyl ester groups were twisted from the ring planes by 4.3(4)° and 3.3(4)°. The bond lengths of the azulene systems, from 1.374(8) Å to 1.410(8) Å, did not show significant differences within their standard deviations in both the molecules. This was the same order of magnitudes as found by Kaftory et al.[37] for other substituted azulene derivatives. Only both bonds between the bridgehead atoms in **112** are considerably longer, C3A-C8A 1.507 (6) Å and C3A'-C8A' 1.495(7) Å.

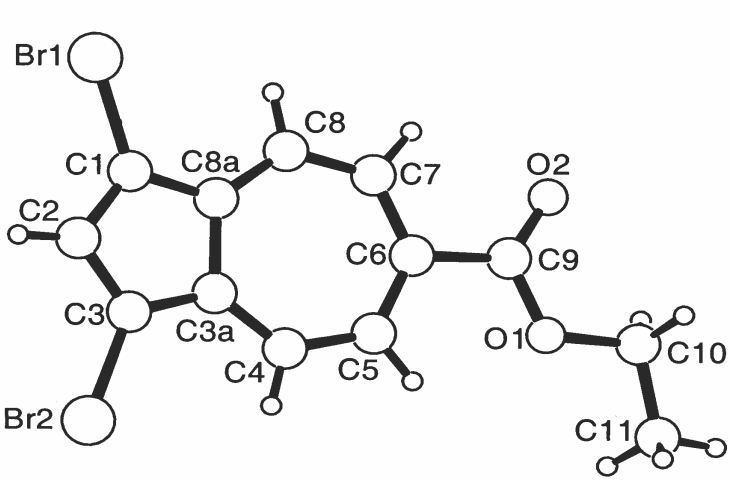
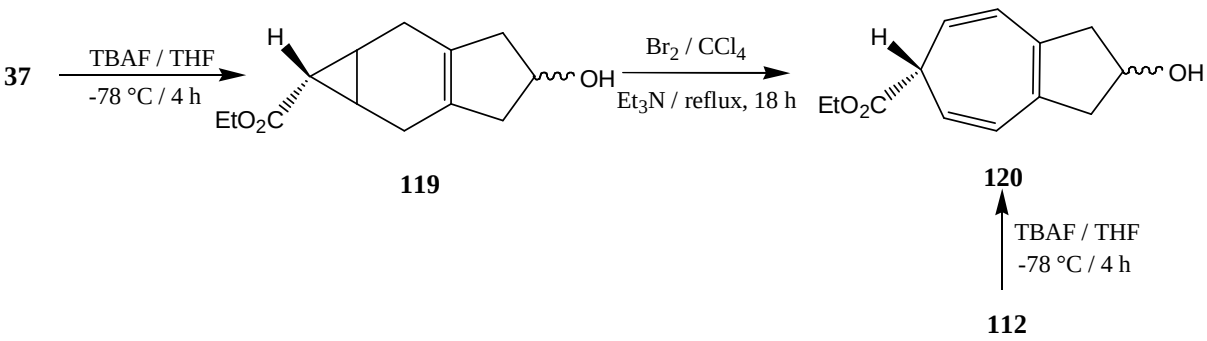


Figure 11. Structure of **113** in the crystal.[74]

2.7.1. Deprotection of TBDPS ethers 37/112

Considering compound **120** as an intermediate for further coupling reactions, it was thought desirable to remove the TBDPS group without damaging the rest of the molecule. After trying various approaches,[75] the method reported by Overman et al.[76] was found to be the method of choice where a more expensive but effective commercially available catalyst, tetrabutylammonium fluoride (TBAF) in THF, was used, resulting in almost quantitative yield of **119** from **37**. However, deprotection of **112** to **120** did not give promising results (~50 % yield). Therefore, the ring expansion strategy as described before was employed to obtain **120** from **119** in above 60 % yield of the final product.

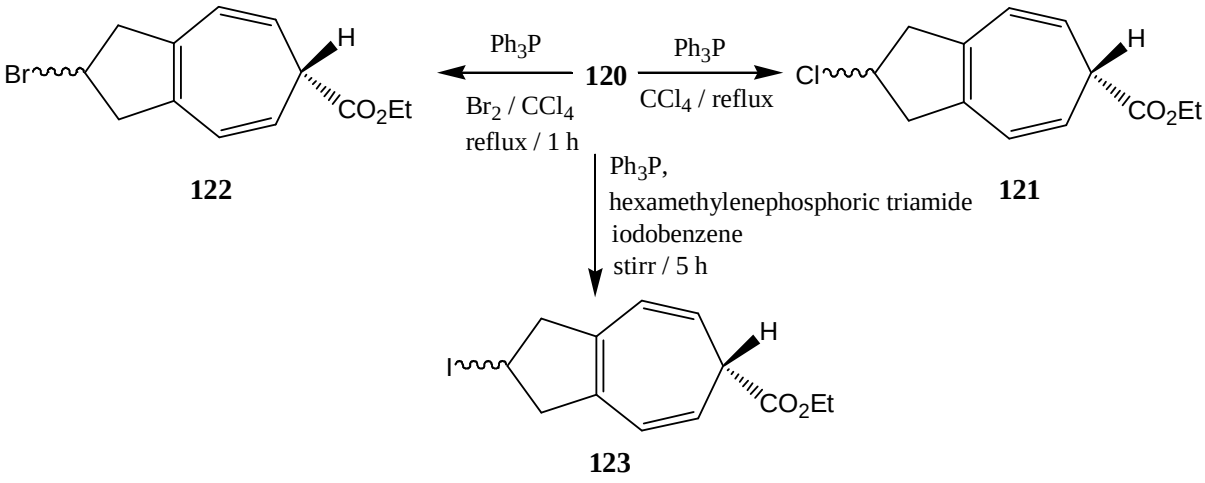
The disappearance of aromatic signals at 7.69-7.41 ppm and signals at 1.07 ppm due to *t*-butyl protons in ^{1}H spectrum indicated the formation of **119**. Compounds **119** and **120** were further characterized by their usual spectroscopic and analytical data which are given separately in the experimental section. The stereochemistry in case of **119** and **120** is supposed to be the same as mentioned earlier for **37** and **112**.



Scheme 40. Synthetic route to cycloheptatriene **120**

2.7.2. Halogenation of 120

Derivative **120** is in principle an important candidate for various coupling reactions. However, most of such reactions are successful only for activated molecules[77] and the most promising results were obtained with an intermediate having halogen substituents. Therefore, halogen derivatives of **120** are important intermediates and the method of choice for the conversion of the alcohol to halogen derivatives utilizes Ph_3P and corresponding halogen.[78] Alcohol **120** was converted to the halogenated derivatives **121-123**. It is important to note that the reaction in the cases of chloride and iodide resulted in ~60 % yield but in the case of bromide only ~30 % of the purified product **122** could be isolated. Direct conversion[79] of the protected alcohol **112** to bromide derivative **122** did not yield any product at all. All of these derivatives showed similar ^{13}C NMR spectra, however, signals corresponding to 2-H in the ^{1}H NMR spectra appeared to have slightly different ppm values (δ = 4.57 ppm for the bromo derivative, δ = 4.60 ppm for the chloro derivative and δ = 4.76 ppm for **123**). All of these derivatives were fully characterized further by their usual mass spectrometric and other analytical data which are given separately in the experimental section. The stereochemistry at position 6 of all these halogen derivatives is supposed to be the same as mentioned earlier for **120**, however, their stereochemistry at position 2 remains to be established.



Scheme 41. Halogenation reactions of the alcohol **120**

2.7.2.1. Attempted coupling reactions of the halides 122 and 123

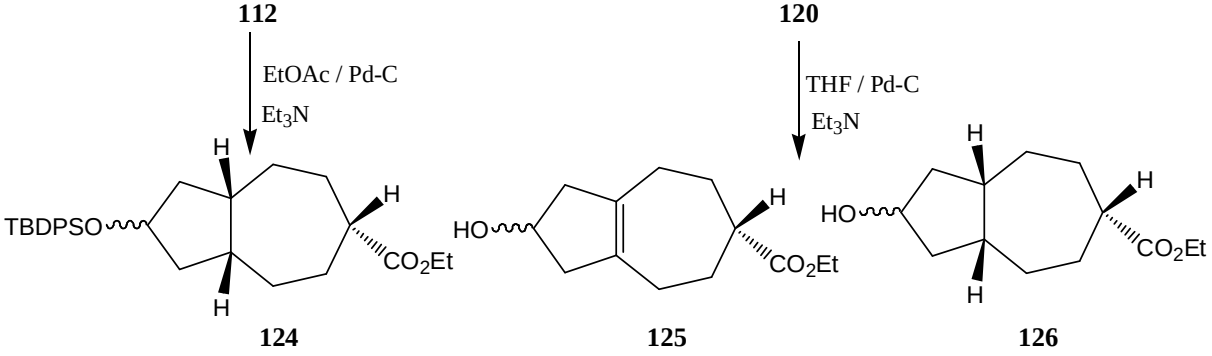
Having prepared the halogen derivatives of **120**, various coupling reactions[80] were tried. In most cases starting material was recovered and in several cases cleavage of halogen resulted in the formation of conjugated double bonds. The details of all these reactions are summarized in Table 2.

Expt.	Halogen	Reagent	Other conditions	Results
1	Br	Li	THF, ultrasound	Starting material recovered
2	Br	MnO_2 , $CuCl_2$	THF / water (3:1)	No reaction
3	Br	In	DMF, reflux	Mixture of products
4	Br	MnO_2 , $CuCl_2$	THF, ultrasound	Mixture of products
5	I	In	DMF, reflux	Starting material and some unknown substance
6	I	MnO_2 , $CuCl_2$	THF / water (3:1)	Starting material recovered

Table-2. Attempted coupling reactions of **122 / 123.**

2.7.3. Hydrogenation of 112 and 114

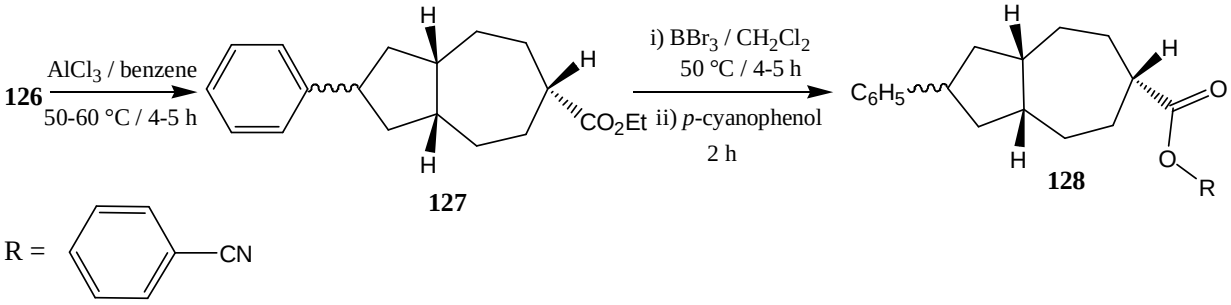
The failure to coupling reactions lead to a modification of the synthetic strategy. Thus, first reduction of compounds **112** and **120** was carried out to avoid the problem, if at all, due to the presence of double bonds during coupling reactions. Keeping in mind that the presence of acidic media could cleave the hydroxyl group during hydrogenation, basic conditions were employed and the use of triethylamine and THF in case of **120** yielded a mixture of **125** and **126** in almost quantitative yield while in case of **37**, EtOAc was used as solvent resulting in 93 % yield of pure **124**. The presence of a singlet at δ = 127.7 ppm in the ^{13}C NMR spectrum indicated the presence of double bond between C-3a / 8a in **125** while the appearance of a doublet at about 42.6 ppm in **124** and **126** indicated its absence. It is again important to note that the hydrogenation in the absence of triethylamine did not give the desired results, probably due to the reason given above. The stereochemistry of compounds **124-126** is supposed to be the same as mentioned earlier for **73** and **74**; their complete spectroscopic and analytical data can be found in the experimental section again.



Scheme 42. Hydrogenation of **112 / 120**

2.7.4. Synthesis of ester 128

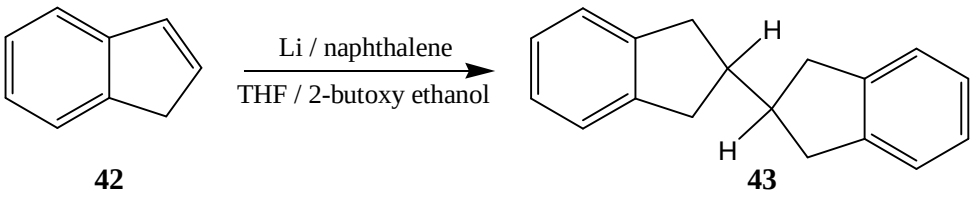
Compounds **124-126** were considered as an excellent choice for a variety of new materials to be used as liquid crystals. Therefore, efforts were under taken towards the synthesis of **128** to test its mesogenic properties. Under Friedel-Crafts alkylation conditions, it was possible to synthesise **127** as a clear liquid, although not in good yield (20 mg, 38 %). Transesterification of **127** in the presence of BBr_3 in CH_2Cl_2 and *p*-cyanophenol yielded **128** as a light yellowish liquid. The disappearance of a triplet in the ^1H NMR spectrum for -CH_3 protons and the appearance of one multiplet at δ = 7.58-7.61 ppm corresponding to 12/14-H protons indicated the presence of the new ester **128**. Derivatives, **128** was fully characterized by its other spectroscopic and analytical data given separately in the experimental section while its stereochemistry at position 6 and at ring junction is supposed to be the same as discussed earlier for **124** and **126**; however, ist stereochemistry at position 2 remains to be established. It was found that during the course of the reaction the amount of $AlCl_3$ played a critical role in the over all yield of the final product **127**, and 2.2-2.4 equivalents of $AlCl_3$ resulted in the best yield in this case.



Scheme 43. Synthesis of ester **128**

2.8. Synthesis of 2,3,2',3'-Tetrahydro-1*H*,1'*H*-[2,2']biindenyl 43

Continuing the synthetic strategies to prepare columnar materials with replaceable terminal groups, **43** was selected as another target as it was supposed to extend the length of the molecule to get the desired materials expected to possess novel mesogenic properties. In the literature there are only a few references for the synthesis of 2,3,2',3'-Tetrahydro-1*H*,1'*H*-[2,2']biindenyl[81] and the yields are usually poor. The most promising method[82] couples indene with itself using lithium and naphthalene in THF as the initiators and ethylene glycol monobutyl ether as a terminating agent. By using 2-butoxyethanol as the terminating agent it was possible to synthesise and separate **43** as a colourless solid which was recrystallized from dichloromethane and pentane to get colourless needles suitable for X-ray analysis.



42 **43**

Scheme 44. Synthesis of 2,3,2',3'-Tetrahydro-1*H*,1'*H*-[2,2']biindenyl (**43)**

2.8.1. Theoretical approach to 2,3,2',3'-Tetrahydro-1*H*,1'*H*-[2,2']biindenyl 43

As stereochemistry plays a vital role for the new materials to be liquid crystals, it was considered initially more interesting in defining the exact stereochemistry of the 2,3,2',3'-Tetrahydro-1*H*,1'*H*-[2,2']biindenyl core at position 2 and 2'. Therefore, density functional theory of BLYP was applied to find the most stable stereoisomer. A relaxed surface scan was computed using the B3LYP[83] hybrid density functional in combination with the 6-31G (d) basis set as implemented in the Gaussian program.[84] The central C-C bond was rotated around 360° in 10° steps. At each step, all other internal degrees of freedom were optimized. The resulting energy plot is shown in Figure 12. The global minimum (C_{2h} symmetry; staggered/*trans*) was separated by a barrier of ~ 5 kcal/mol from a second minimum (C_2 symmetry, staggered/*cis*). The second barrier, leading to an energy maximum (C_{2v} symmetry, eclipsed, *cis*) connects the two degenerate local minima (Figure 12).

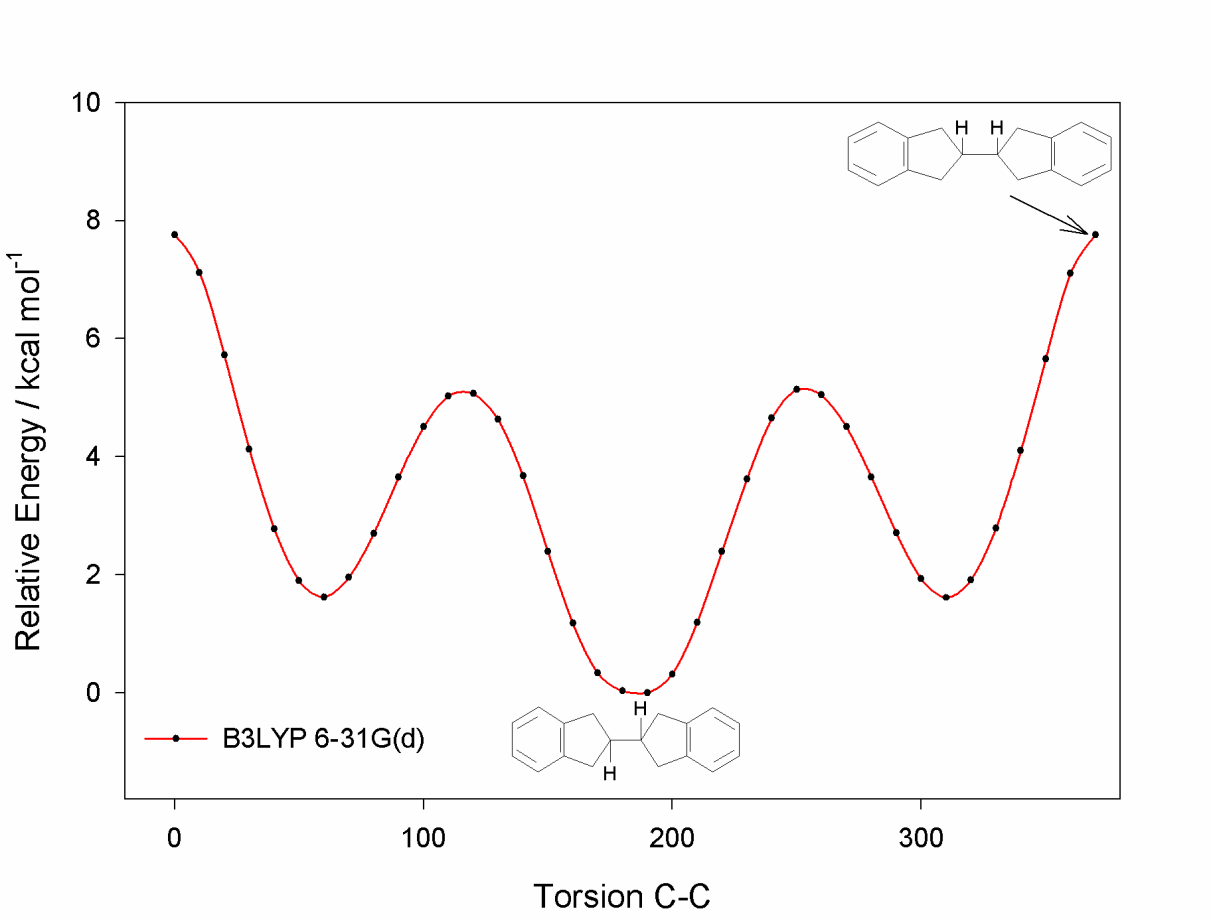


Figure 12. Potential energy surface for 2,3,2',3'-Tetrahydro-1*H*,1'*H*-[2,2']biindenyl **43**

2.8.2. Experimental (X-ray analysis) approach to 43

Compound **43** was recrystallized from CH_2Cl_2 and pentane to yield colourless needles suitable for X-ray analysis. The five membered ring system of the indan skeleton was found to have an envelope shape. Two disordered positions were found for the top atom C2 (Figure 13 shows only one of the two disordered positions) pointing in two opposite directions with folding angles of 22.9 (2°) and 11.0 (3°). Our observations are in accordance with chemical or theoretical view points. In the indan crystal, disorder position at 2 and 2' could develop *cis*- or *trans*-arrangements. However, the *cis*-arrangement is not favoured due to the following reasons: **a)** in the *cis*-arrangement the C2-C2A' single bond would be too short with 1.418Å while in the *trans*-arrangement C2-C2' is 1.546Å and for C2A-C2A' as 1.477Å which is acceptable for a C-C single bond on a disorder position; **b)** *cis*-arrangement would develop hydrogen bonding of the value of 1.64Å which would be very short and thus seemed unrealistic; **c)** in the *cis*-arrangement an energetically unfavourable eclipsed conformation would develop. Therefore, the possibility of a *cis*-conformation can be excluded.

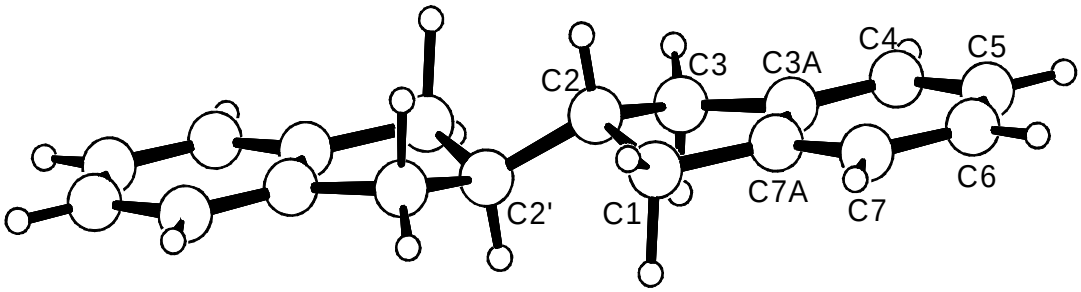


Figure 13. Structure of **43** in the crystal

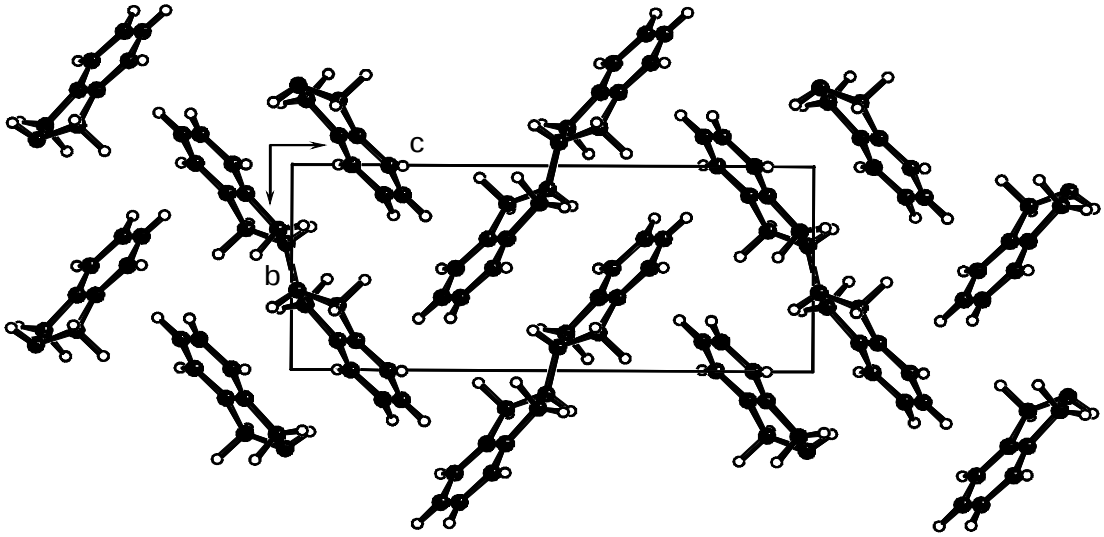
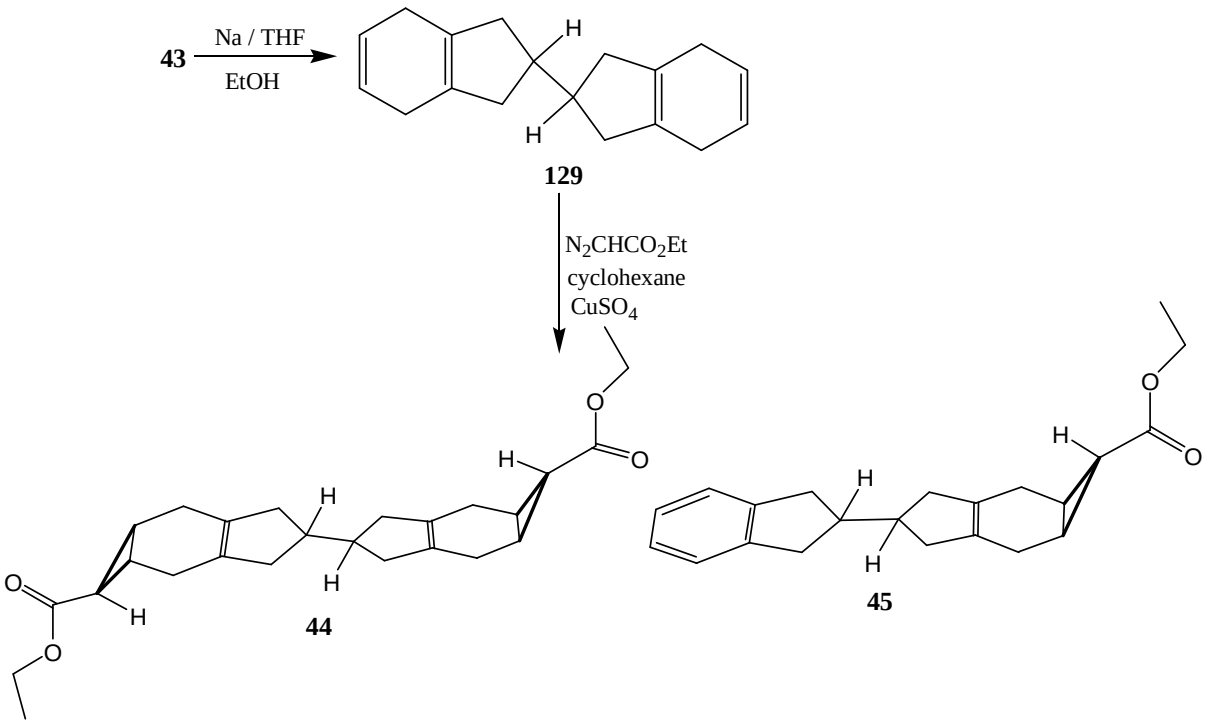


Figure 14. Packing diagram of **43**; view along the crystallographic a-axis.

2.8.3. Synthesis of diester 44 from 43

After confirming the stereochemistry of **43**, attempts were undertaken to extend the length of the molecule in order to get materials which could be used as precursors for liquid crystals and the simplest approach was via Birch reduction of **43** and subsequently carbene addition followed by ring expansion as mentioned earlier. Birch reduction of **43** proceeded well (yield ~80 %) in a dilute solution of THF and EtOH due to poor solubility of **43** and provided **129** as a colourless solid. The mono-reduced compound (with only one benzene ring reduced), was always observed as a side product. The raw **129** was subjected to carbene addition to get the diester **44** as a colourless solid. Due to the poor solubility of **129**, excess solvent was used again, and in addition to diester **44**, the monoester **45** was also separated and characterized as a side product. The purification of **44** was carried out by column chromatography on silica gel. The less polar **45** eluted first, the raw **44** followed next and was later liberated from the co-formed diethyl fumerate by washing with small amounts of pentane. The presence of a singlet at 2.55 ppm and another singlet at 5.68 ppm in ^{1}H NMR spectrum for 4,7-H and 5,6-H respectively in **129** and the presence of a quartet at 4.15 ppm and a triplet at 1.29 ppm both

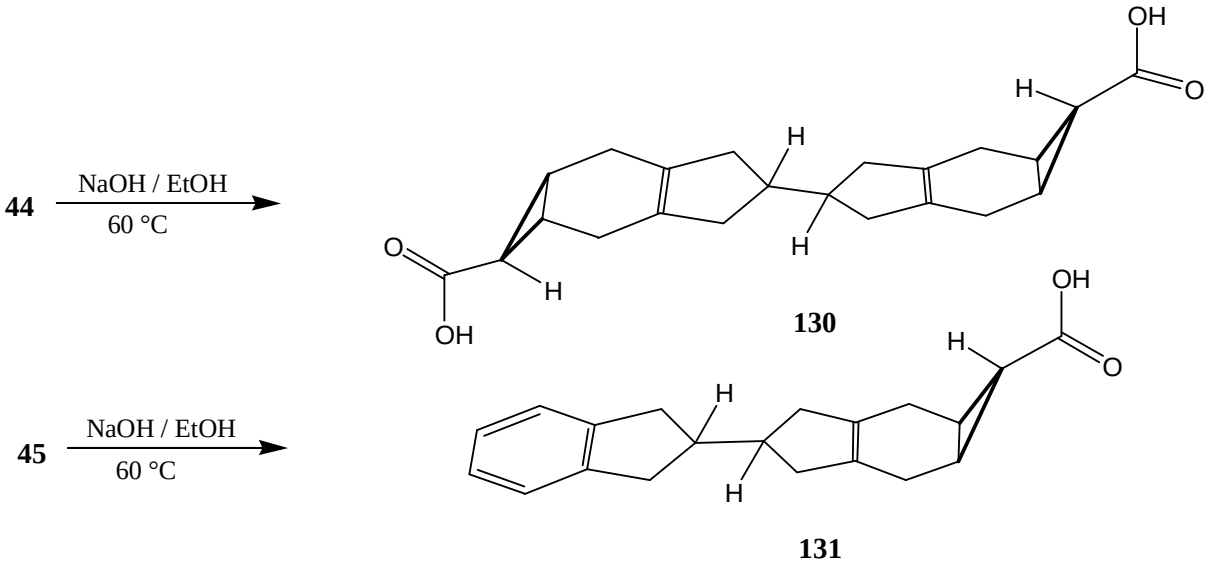
with coupling constants of 7.1 Hz in ^{1}H NMR spectrum for 8-H and 9-H respectivey in **44** and **45** indicated the formation of these compounds. Compounds **129**, **44** and **45** were further characterized by their usual analytical data which are given separately in the experimental section.



Scheme 45. Synthetic route to diester **44**

2.8.3.1. Hydrolysis of 44 and 45

To investigate the exact stereochemistry of **44** and **45**, both esters were hydrolysed hoping that the resulting acids could be more easily investigated by X-ray analysis. The acids **130** and **131** were obtained by stirring **44** and **45** separately with 1M NaOH in ethanol. Because of the low solubility of the starting materials, the mixture had to be heated to 60 °C for complete dissolution. The acid **130** was obtained as a colourless solid sparingly soluble in methanol and DMSO and in acetic acid it gave clear solution on warming, while acid **131** was obtained as a lightly coloured solid soluble in any polar solvent.



Scheme 46. Synthetic route to diacid **130** and its monoacid analog **131**

Being of high symmetry, diacid **130** was sparingly soluble even in DMSO, therefore, it could not be recrystallized, while monoacid **131**, which was obtained in the form of white flakes, was recrystallized from hexane and dichloromethane to yield pure crystals suitable for X-ray analysis. Both of these acids were fully characterized by their usual spectroscopic and analytical data given separately in the experimental section.

As shown in Figure 15, the cyclohexene ring is slightly twisted by 0.1(2)° to 18.1(4)°. The cyclopropyl group is strongly folded to its neighbouring plane of the six-membered ring by 72.4(1)° to 72.7(1)°. The carboxylic group is in the *exo* position with a bisecting orientation of the carbonyl group to the three membered ring (89.5(1)° and 88.9(1)°). As a result of this nearly optimal orbital overlap, relatively long vicinal bonds from 1.524(4) Å (C12-C15), to 1.522(4) Å (C13-C15) and short distal bonds, 1.486(4) Å (C12-C13) in the cyclopropyl subunit were found.

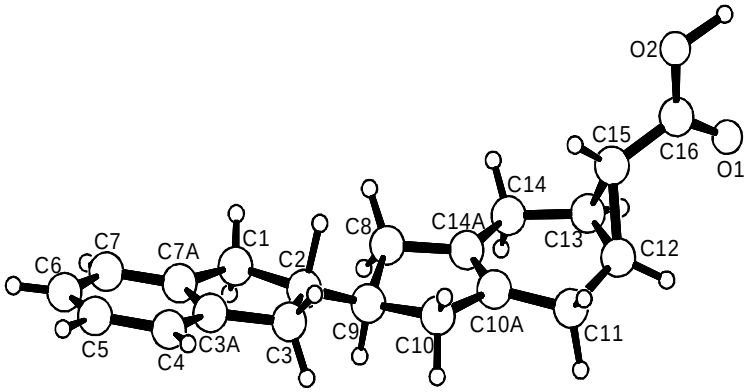
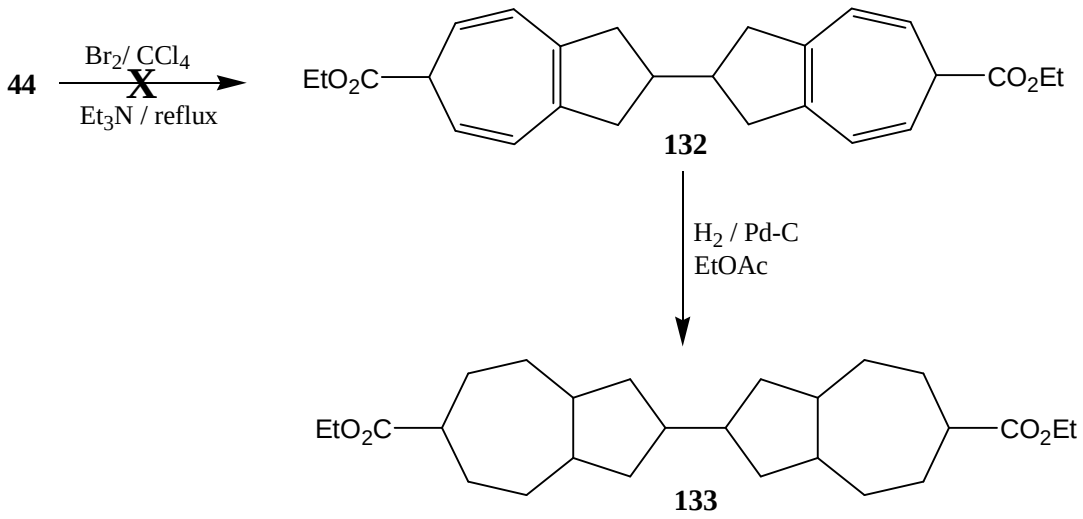


Figure 15. Structure of **131** in the crystal; only one of the disordered positions of C9 is shown.

2.9. Attempted synthesis of target molecule 132

Our aim to synthesise columnar materials to be used as precursors for liquid crystals lead us to devise a synthetic strategy ending at target molecule **132** and its hydrogenated derivative **133** which in principle could be novel intermediates for further transformations because they possess replaceable terminal groups. After synthesising **44**, attempts were focused on the ring expansion strategy as mentioned earlier to get **132**. Due to the symmetrical nature of **44** solubility problems were encountered which were solved by working in very dilute solutions. Later, all attempts resulted in very complex mixtures of products from which the desired molecule could not be isolated. Therefore, this route to extended systems was abandoned.



Scheme 47. Attempted route to the dimeric diester **133**

2.10. Investigations of some liquid crystalline properties of the new materials

After synthesising and determining the exact stereochemistry of the various new materials based on the perhydroazulene ring system, their liquid crystalline behaviour was investigated. The thermal behaviour of a selection of the new materials was investigated by polarizing microscopy and by differential scanning calorimetry (DSC) and later by X-ray examination.

DSC measurements were carried out for compounds **76**, **77**, and **104**. The first heating curve in the DSC of **76** showed phase transition at about 51°C with phase transformation enthalpy of 21 kJ/mol which is typical for phase transition from crystalline to liquid. A transition from liquid crystalline to isotropic liquid, which is very sharp and with a typical enthalpy of transition of about 1 kJ/mol, could not be observed. In the first cooling curve no phase transition was observed which could be due to super-cooling effect. In case of **77** two phase transitions with an enthalpy of transition from 4 to 5 J/mol, which is too small for melting and too large for heating of mesophase transformation, were observed. Compound **77** when observed under the microscope at 30 °C, showed a visible smectic phase texture. However, some exact textural features of both materials could not be observed when measured by polarizing microscopy at various temperatures. The DSC investigation in case of **104** also showed a clear phase transition but could not yield some textural features when observed under polarizing microscope.

The common feature in all of the above mentioned compounds was their *cis*-fused ring system. Further investigations concerned the mesogenic properties in both stereoisomers i. e. *cis*-.and *trans*-fused ring systems. For this purpose two more derivatives, **81** and **83** with different stereochemistry were investigated for their liquid crystalline properties. Compound **81** did not show any phase transition temperature in DSC measurements. However, compound **83** showed the enthalpies of phase transition.

On heating, **83** transformed to the isotropic phase at about 104 °C. The crystals started to melt at about 79 °C on heating. Compound **83** showed a melting transition at 89.3 °C (peak temperature, enthalpy 15.9 kJ mol^{-1}) and a transition from nematic phase to isotropic at 104.6 °C (enthalpy 2.0 kJ mol^{-1}).

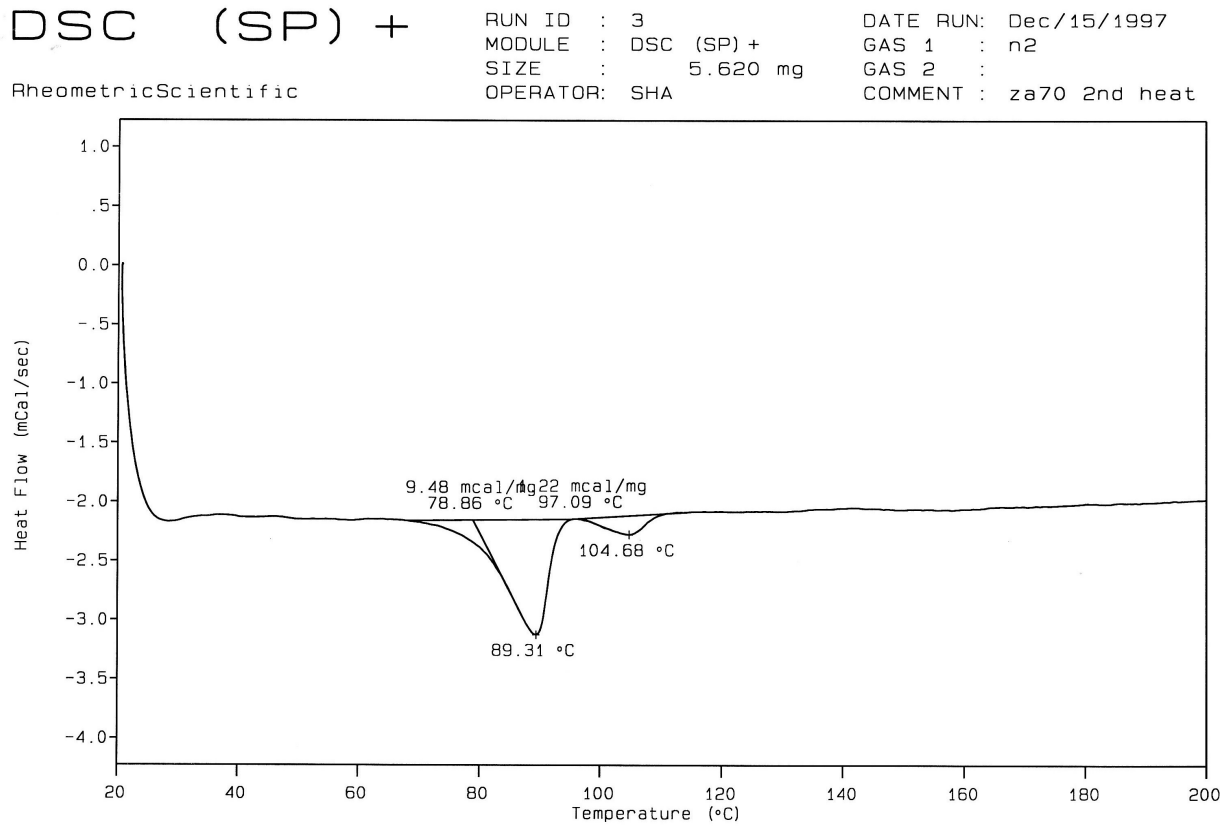


Figure 16. DSC curve of **83** (2nd heating) showing phase transition temperatures

Compound **83**, when observed under polarizing microscopy, exhibited textural features of a nematic phase. On heating the compound, typical schlieren and thread textures were observed indicating the nematic nature of material (Figures 17 and 18).

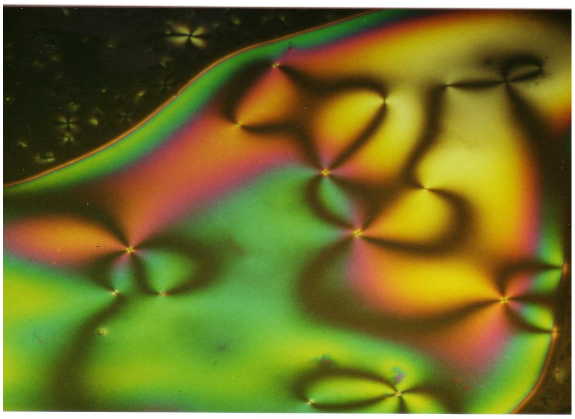


Figure 17. Schlieren texture of **83**

Figure 18. Thread texture of **83**

Figures 17 / 18. Optical texture of **83**. Photomicroscopic images of the mesophase were obtained with a polarizing microscope (Olympus BX50 system)

The above textures were also observed on second heating (Figure 19).

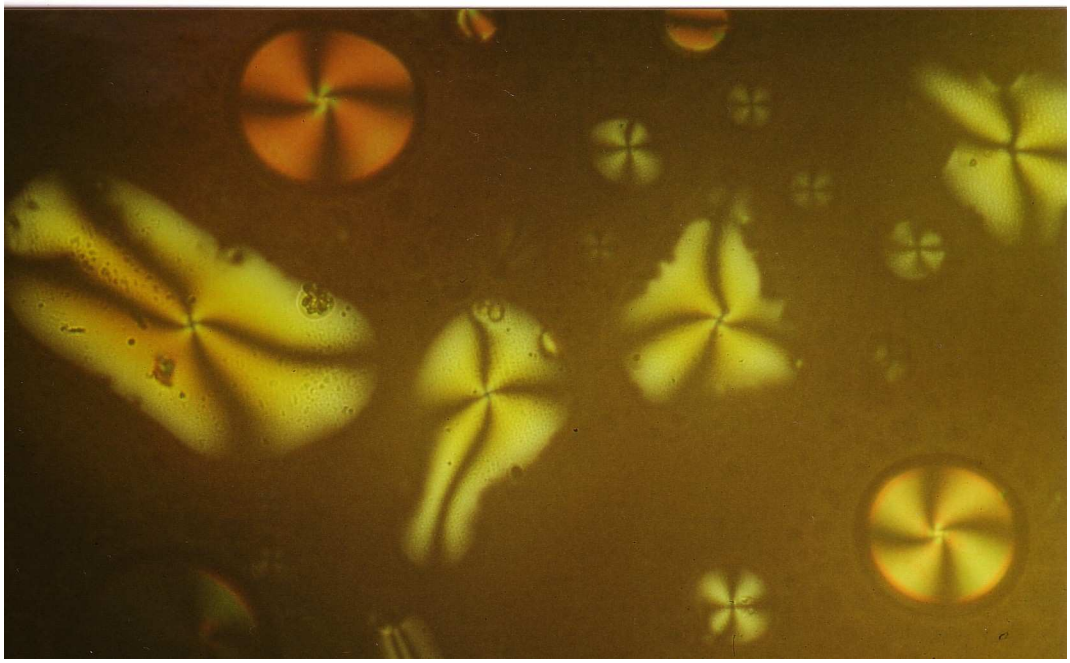


Figure 19. Optical texture (droplets) of **83**. Photomicroscopic image of the mesophase was obtained with a polarizing microscope (Olympus BX50 system.

Small angle reflections (X-ray analysis) between 180 + 122° were measured to investigate more about the liquid crystalline properties of **83**. At 110 °C (Figure 20) only a nematic phase exists while very weak small angle reflexs indicate smectic fluctuations.

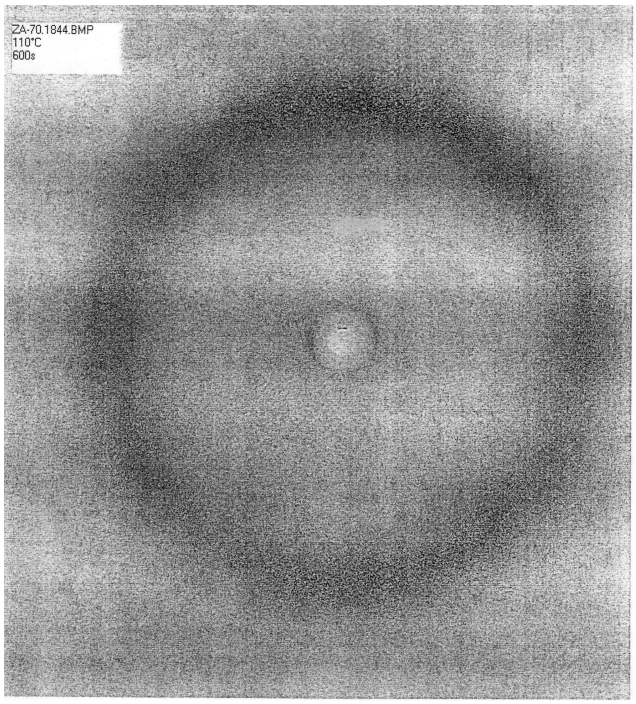


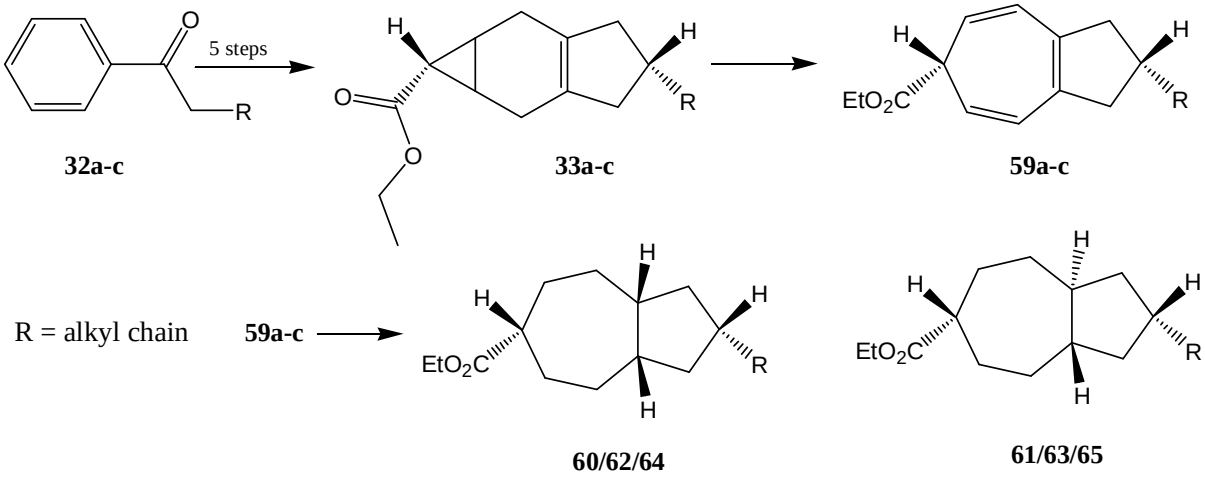
Figure 20. Small angle reflexes (X-ray analysis) of **83** at 110 °C showing nematic phase.

In order to investigate some more materials for their mesogenic properties, compounds **60**, **44**, **78**, **79**, **82**, **85**, **97**, **130** and some acid derivatives of perhydroazulene system were examined under microscope and then their DSC studies were done. However, no promising results were found regarding their enthalpies of transition and textural features of typical nematic or smectic phases.

3. Summary

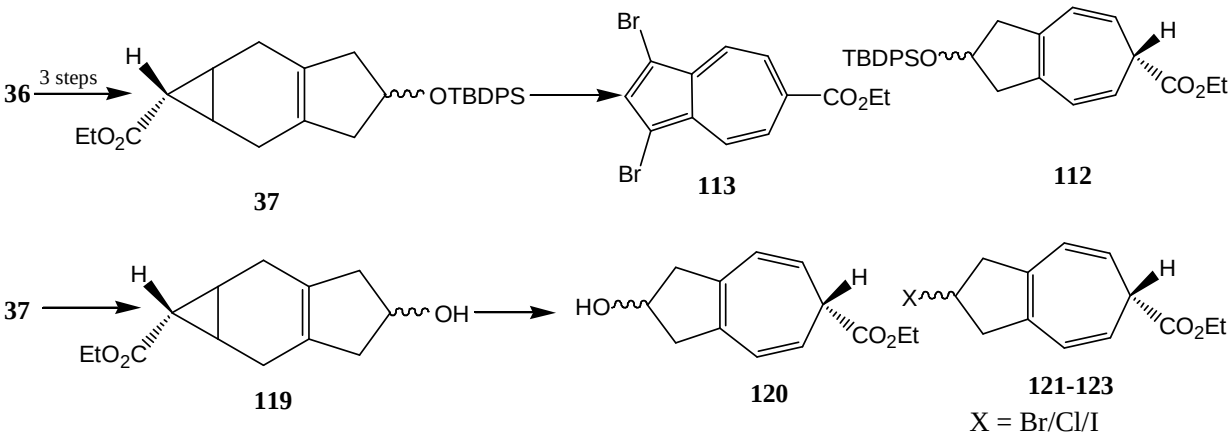
The aim of this work was to synthesise the perhydroazulene ring system with substituents in position 2 and 6, to determine the stereochemistry of these novel derivatives, and finally to investigate the mesomorphic properties of these compounds. It was supposed that the perhydroazulene ring system would be analogous to the cyclohexyl ring and would represent an important and effective nematogenic building block. It was expected that the new phenylhydroazulenes would have low viscosities compared with phenylcyclohexanes resulting in a new class of materials with potential LC applications.

3.1. In the first part of this work, the perhydroazulene ring system was constructed and its stereochemistry at ring junction and at 2 and 6 position was determined with the help of a molecular mechanics approach and various crystal structures of their acids. The synthesis of the perhydroazulene started from simple benzene derivatives with promising overall yields of **59a-c** where R represents alkyl chain with carbons 3-5. The catalytic hydrogenation of **59a-c** resulted in quantitative yields of perhydroazulene systems **60-65**. The effect of various solvents on the hydrogenation of **59a-c** to various *cis*-and *trans*-fused systems was determined.

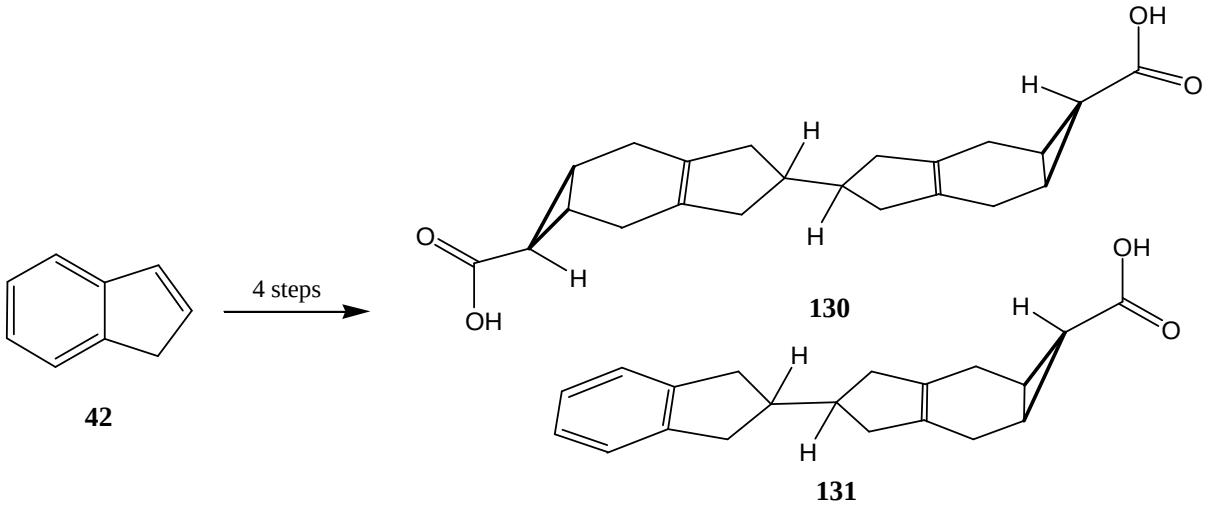


3.2. To obtain a perhydroazulene ring system where the substituent pattern at position 2 could be changed, a new route was developed to reach a perhydroazulene system with different replaceable terminal groups at position 2. Therefore, compounds **112** and **113** were synthesised starting from commercially available **36** in promising yields. The removal of protecting group from **112** yielded compound **120** which was further converted to various halogen derivatives **121-123**. It was also possible to obtain **120** from **119** by the ring

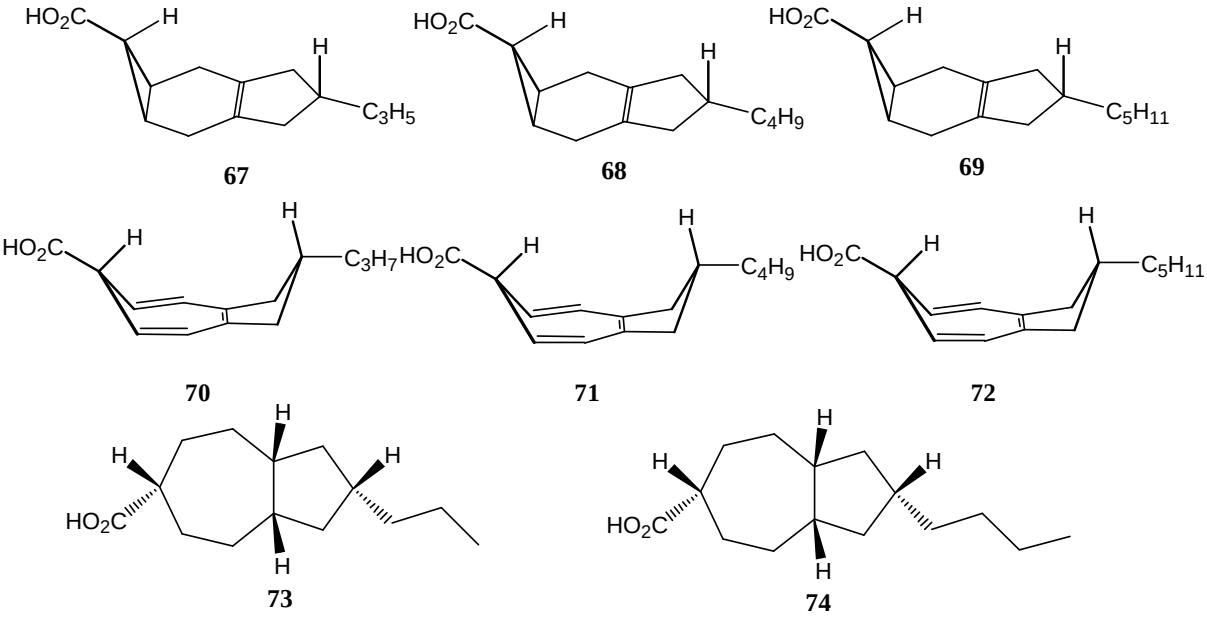
expansion strategy. The compounds **121-123** are considered to be the important candidates for various coupling reactions.



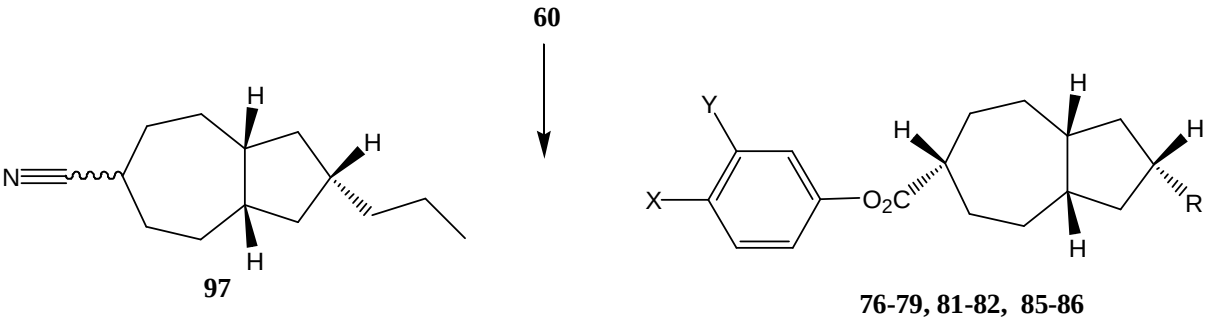
3.3. In the third part of this dissertation, compounds with longitudinal structures like **130** and **131** were synthesised starting from very simple commercially available indene. Stereochemical features of these bisindan were investigated by density functional theory (Figure 12) of BLYP. A relaxed surface scan was done using the B3LYP hybrid density functional in combination with the 6-31G (d) basis set as implemented in the Gaussian program and further by an X-ray analysis of 2,3,2',3'-Tetrahydro-1*H*,1'*H*-[2,2']biindenyl (Figure 13) and acid **131** (Figure 15).



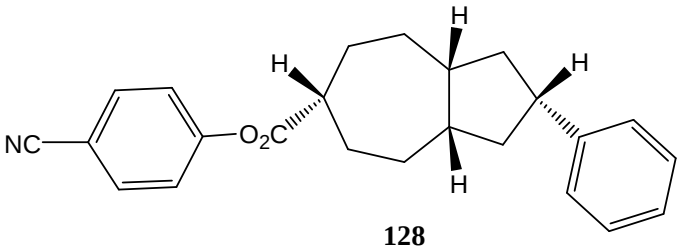
3.4. In the fourth part of this investigation, acids **67-69**, **70-72** and **73/74** were synthesised, recrystallized and their stereochemical features confirmed by X-ray analysis.



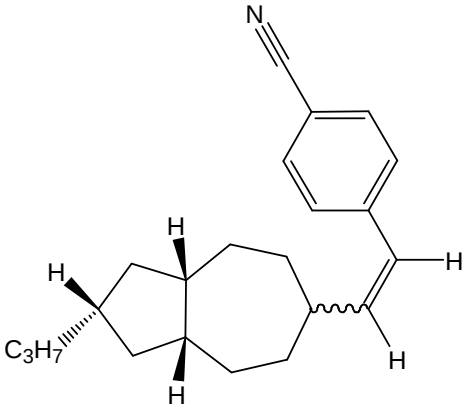
3.5. In the fifth section of this work, new derivatives based on the perhydroazulene system were synthesised. Various synthetic strategies were employed to get the new materials with *cis*- and *trans*-fused perhydroazulene ring systems. Some of the new materials were recrystallized in order to get suitable crystals for X-ray analysis and subsequently their X-ray data confirmed the stereochemistry of the new materials. New materials with an ester linkage between the perhydroazulene system and the phenyl derivative and also with direct connection between both systems were synthesised. A nitrile where the CN group is directly attached to the perhydroazulene system was synthesised as it was expected to show novel mesogenic properties.



As materials with interconnecting ethylene bridge show mesomorphic properties, compounds like **104** was synthesised by Wittig coupling starting from 2,6-substituted perhydroazulene system. It was also supposed that the insertion of a difluoromethylene bridge into the core structure of perhydroazulene system like **104** could result into a class of materials with dramatic changes in all mesomorphic properties; therefore, attempts were made to synthesise difluorooxymethylene bridged systems. For the extension of ring system, Friedel-Crafts alkylation reaction was employed to synthesise new materials like **128**.



128



104

3.6. In the last part of the present work, the newly synthesised materials were investigated for their mesogenic properties with the help of DSC and polarizing microscopy. Some promising results were found for compounds **76**, **83** and **104** while others, **77**, **78**, **79**, **82**, **85**, **86** and **128** did not show very unusual enthalpies of transition and textural features.

4. Experimental

4.1. Instrumentation and general experimental considerations

Thin layer chromatography (TLC):

Thin layer chromatography was performed by using precoated plastic plates, PolyGram Sil G/UV_{254}.

Column chromatography:

Column chromatography was performed on Silica gel 60 (70-230 mesh) from Merck (Darmstadt).

Melting points:

Measurements below 200 °C were determined on a Büchi 510 melting point apparatus and above 200 °C were carried out on a Kofler-Heiztischmikroskop apparatus and are uncorrected.

NMR spectroscopy:

^{1}H and ^{13}C NMR spectra were recorded on the following spectrometers;

Bruker AC 200, ^{1}H NMR (200.1 MHz); ^{13}C NMR (50.3 MHz);

Bruker DRX-400, ^{1}H NMR (400.1 MHz); ^{13}C NMR (100.6 MHz);

Chemical shifts (δ) are expressed in parts per million (ppm) downfield from tetramethylsilane or using the residual non-deuterated solvent as internal standard ($CDCl_3$: ^{1}H: $\delta = 7.26$; ^{13}C: $\delta = 77.00$). Coupling constants are expressed in Hertz.

IR spectroscopy:

IR spectra were recorded using a Nicolet 320 FT-IR and a Bruker Tensor 27 spectrometer. Samples were prepared either as KBr pellets or as thin films. Band positions are reported in reciprocal centimetres. Band intensities are characterized by the following symbols; vs (very strong), s (strong), m (medium), w (weak).

UV / Vis spectroscopy:

UV spectra were recorded in acetonitrile and methanol using a Beckman UV 5230 and HP 8452 A Diode Array spectrophotometer.

Mass spectrometry:

Mass spectra were recorded using a Finnigan MAT 8430 spectrometer using the electron ionization method (EI, 70 eV).

GC/MS:

GC/MS spectra were recorded on a Finnigan MAT 4515 (EI, 40 eV) mass spectrometer attached to a Carlo-Erba HRGC 5160 (DB 1-0.25 μm-fused-silica capillary column; 30m x 0.31 mm ID; carrier gas Argon) gas chromatograph.

Elemental ynalysis:

Elemental analyses were carried out at the Institut für Pharmazeutische Chemie, TU Braunschweig.

DSC measurements:

DSC analyses were performed using a DSC Rheometric Scientific DSCSP. All compounds were studied at various scanning rates (5 and 10° min^{-1}) under nitrogen.

Microscopic analysis:

Optical textures (Photomicroscopic images) of the mesophases were obtained with a polarizing microscope (Olympus B x 50 system) equipped with a Linkam-LTS-350 variable temperature stage.

X-ray analysis:

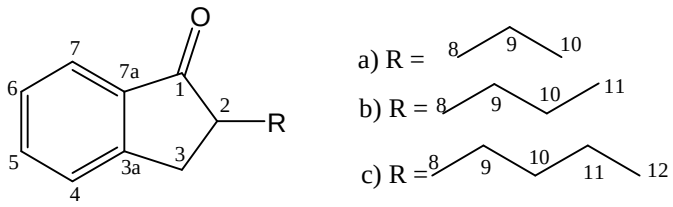
X-ray data were obtained on a Siemens R3; Stoe STADI-4; Bruker AXS SMART 1000 CCD, Bruker SMART APEX diffractometers. Data collections and reductions were performed with the BRUKER SMART and SAINT software. A semi-empirical absorption correction (SADABS) was applied to certain compounds and structure refinement were carried out with SHELXS 86, SHELXL 97 and by direct methods (SHELXTL). Mo-K_α rays with wavelength 71.073 were used. The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The hydrogen atoms at the acyclic methylene groups were refined with a 'riding' thermal parameter while all other H atoms were refined isotropically. Carbon atoms with 15 % multiplicity were all refined isotropically.

Drying of solvents:

CH_2Cl_2 and Et_3N were distilled from CaH_2 under nitrogen prior to use while THF and Et_2O were distilled from Na and benzophenone under nitrogen prior to use. All other chemicals were of reagent quality and used as obtained from the manufacturers. Reactions were carried out in dry N_2 when necessary.

4.2. Experimental procedures

4.2.1a. 2-Propyl-indan-1-one (52a)



52a-c

A mixture of valerophenone (25 g, 0.154 mol), hexamethylenetetramine (36 g, 0.26 mol) and acetic anhydride (34 g, 0.33 mol) was heated at 80 °C for 5 h under nitrogen atmosphere. The reaction mixture was cooled to 30 °C and poured into a stirred mixture of dichloromethane (150 mL) and sodium hydroxide (150 mL of a 2N solution). The organic layer was separated and washed with aqueous HCl (80 mL of 1 N solution). The CH_2Cl_2-solution containing the product, 2-propyl-1-phenyl-2-en-1-one, **51a-c** was azeotropically dried by distilling the CH_2Cl_2 to approximately 50 mL. The solution was used without further purification in the next step. It was added to conc. H_2SO_4 (110 mL) at a rate such that the reaction temperature was maintained between 50-60 °C. The solvent was removed by distillation and nitrogen sweep as soon as it was added. The reaction mixture was stirred at 50-60 °C for 1 h, cooled to 20 °C and quenched with a stirred mixture of CH_2Cl_2 (150 mL) and water (150 mL). After separating the aqueous layer the organic layer was concentrated in a rotary evaporator, dried with $MgSO_4$ and filtered through silica gel to produce 18 g (67 %) of 2-propyl-indan-1-one **52a** as light yellow oil.

R_F (SiO_2; pentane/CH_2Cl_2; 6:4) = 0.5

B. p. = 108-110 °C / 5 mm (Lit.[49b] 110 °C / 5 mm)

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.95 (t, ^3J = 7.1 Hz, 3 H, 10-H), 1.39-1.48 / 1.90-1.94 (m, 4 H, side chain protons), 2.61-2.81 (m, 2 H, 3-H), 3.26-3.32 (m, 1 H, 2-H), 7.31-7.35 (m, 1 H, 6-H), 7.42-7.44 (d, ^3J = 7.66 Hz, 1 H, 4-H), 7.53-7.57 (m, 1 H, 5-H), 7.71-7.73 (d, ^3J = 7.64 Hz, 1 H, 7-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 208.77 (s, C-1), 32.64 (t, C-3), 47.05 (d, C-2), 123.55 (d, C-6), 127.06 (d, C-7), 126.35 (d, C-4), 134.39 (d, C-5), 153.56 (s, C-7a), 136.62 (s, C-3a), 13.86 (q, C-10), 20.44 (t, C-9), 33.40 (t, C-8).

IR (film): $\tilde{\nu}$ = 1710 cm^{-1} (s, C=O), 2933, 2960 (s, CH-stretching), 3073, 3033 (w, CH-stretching, aromatic) 1610 (m, C=C aromatic), 1328 (m, CH_3-deformation).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 236 nm (3.42), 250 (4.03), 246 (4.06), 280 (3.26), 288 (3.41), 296 (3.39).

MS (EI, 70 eV): *m/z* (%) = 174 [M^+] (2), 145 [M^+-C_2H_5] (5), 132 [M^+-C_3H_6] (100), 131 [M^+-C_3H_7] (14), 115 [131-O] (12), 103 [131-CO] (6.5).

4.2.1b. 2-Butyl-indane-1-one (52b)

Yield = 18 g, 68 %

R_F (SiO_2; pentan/dichloromethane; 7:3) = 0.28

B. p. = 154 °C / 14 torr (Lit.[49c] 154 °C / 14 torr)

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.94 (t, ^3J = 7.1 Hz, 3 H, 11-H); 1.34-1.53 (m, 6 H, side chain protons), 1.95-2.02 (m, 2 H, 3-H), 2.64-2.71 (m, 1 H, 2-H), 7.30-7.39 (m, 1 H, 6-H), 7.46-7.47 (d, ^3J = 7.71 Hz, 1 H, 4-H), 7.57-7.61 (m, 1 H, 5-H), 7.76-7.78 (d, ^3J = 7.71 Hz, 1 H, 7-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 209.03 (s, C-1), 153.72 (s, C-7a), 136.78 (s, C-3a), 134.53 (d, C-5), 127.21 (d, C-7), 126.46 (d, C-4), 123.76 (d, C-6), 47.37 (d, C-2), 32.79 (t, C-8), 31.09 (t, C-3), 29.51 (t, C-9), 22.63 (t, C-10), 13.89 (q, C-11).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 206 nm (4.51), 242 (4.10), 286 (3.44), 294 (3.43), 248 (4.03), 272 (3.14), 304 (2.79).

IR (film): $\tilde{\nu}$ = 3072, 3031 cm^{-1} (w, C-H stretching, aromatic), 2957, 2858 (s, C-H stretching, aliphatic), 1465, 1434 (w), 1712 (s, C=O).

MS (EI, 70 eV): *m/z* (%) = 188 [M^+] (35), 145 [M^+-C_3H_7] (13), 132 [M^+-C_4H_8] (100), 91 [$C_7H_7^+$] (7), 77 [$C_6H_5^+$] (7).

4.2.1c. 2-Pentyl-indane-1-one (52c)

Yield = 18 g, 88%

R_F (SiO_2; pentan/dichloromethane; 3:1) = 0.4

B. p. = 166 °C / 14 torr (Lit.[49c] 166 °C / 14 torr)

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.85 (t, ^3J = 6.5 Hz, 3 H, 12-H), 1.21-1.50 (m, 8 H, side chain protons), 2.60-2.81 (m, 2 H, 3-H), 3.21-3.30 (m, 1 H, 2-H), 7.30-7.72 (m, 4 H, aromatic protons).

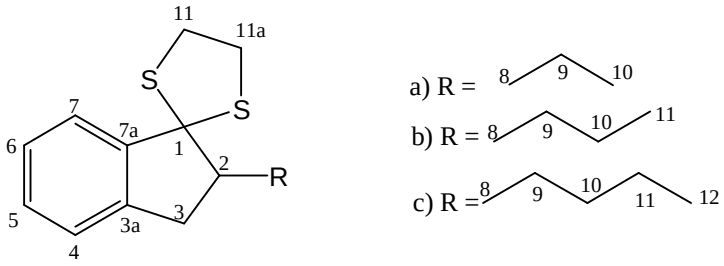
^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.97 (q, C-12), 22.46 (t, C-11), 27.03 (t, C-9), 31.38 (t, C-8), 31.77 (t, C-10), 32.82 (t, C-3), 47.42 (d, C-2), 208.93 (s, C-1), 123.74 (d, C-7), 126.48 (d, C-4), 127.21 (d, C-6), 134.53 (d, C-5), 136.81 (s, C-7a), 153.71 (s, C-3a).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 208 nm (3.99), 242 (3.79), 286 (3.09), 294 (3.09), 204 (3.88).

IR (film): $\tilde{\nu}$ = 3072, 3032 cm^{-1} (w, C-H stretching, aromatic), 2956, 2930, 2871 (s, C-H stretching, aliphatic), 1713 (s, C=O), 1464 (w, C-H deformation).

MS (EI, 70 eV): *m/z* (%) = 202.1 [M^+] (1), 200 [M^+-H_2] (1), 145 [M^+-C_4H_9] (14), 132 [M^+-C_5H_{10}] (100), 131 [132-H] (6).

4.2.2a. Bis-thioacetal of 2-propylindanone (54a)



54a-c

A solution of 2-propyl-1-indanone **52a** (18 g, 0.106 mol) in boron trifluoride etherate (30 g, 27.25 mL, 0.217 mol) was treated with ethandithiol (10.02 g, 0.106 mol) and the mixture stirred at room temp. for 6 h. The mixture was diluted with methanol (60 mL) and the organic layer separated. The solvent was evaporated by rotary evaporation and the residue purified by column chromatography on silica gel with solvents pentane, pentane: CH_2Cl_2 (2:1) to get 18.9 g (71 %) of **54a** as colourless liquid.

R_F (SiO_2; pentane/CH_2Cl_2; 6:3) = 0.8

B. p. = 188-190 °C / 1 torr

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.84 (t, ^3J = 7.2 Hz, 3 H, 10-H), 1.24-1.76 (m, 4 H, side chain protons), 2.37-2.50 (m, 2 H, 3-H), 2.78-2.85 (m, 1 H, 2-H), 3.09-3.42 (m, 4 H, 11 / 11a-H), 6.98-7.39 (m, 4 H, aromatic protons).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.50 (q, C-10), 21.43 (t, C-9), 31.64 (t, C-3), 36.58 (t, C-8), 40.53 / 40.01 (2 x t, C-11 / 11a), 54.50 (d, C-2), 124.25 / 124.38 (2 x d, C-5 / 6), 127.14 / 127.77 (2 x d, C-4 / 7), 140.70 (s, C-1), 148.45 (s, C-3a / 7a).

IR (film): $\tilde{\nu}$ = 3022 cm^{-1} (m, CH-stretching, aromatic), 2956, 2925, 2869 (s, CH-stretching, aliphatic), 1603 (m, C=C conjugated), 1378 (m, CH_3-deformation).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 242 nm (3.39), 232 (2.84), 260 (3.17), 264 (3.16), 272 (3.15), 280 (3.06).

MS (GC / MS): *m/z* (%) = 250 [M^+] (28), 222 [M^+-C_2H_4] (99), 179 [222-C_3H_7] (47), 147 [179-S] (56), 129(62), 115 [179-S_2] (100), 103 [179-CS_2] (8).

4.2.2b. Bis-thioacetal of 2-butylindanone (54b)

Yield = 19 g, 76 %

R_f (SiO_2; entane/CH_2Cl_2; 9:1) = 0.56

B. p. = 216 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.98 (t, ^3J = 6.98 Hz, 3 H, 11-H), 1.39-1.57 (m, 6 H, side chain protons), 2.54-2.68 (m, 2 H, 3-H), 3.05 (m, 1 H, 2-H), 3.30-3.63 (m, 4 H, 12 / 12a-H), 7.57-7.18 (m, 4 H, aromatic protons).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 148.41 (s, C-3a / 7a), 140.68 (s, C-1), 127.72, 127.10 (2 x d, C-4 / 7), 124.31, 124.21 (2 x d, C-5 / 6), 54.62 (d, C-2), 40.95, 40.49 (2 x t, C-12 / 12-a), 36.58 (t, C-8), 30.43 (t, C-3), 29.05 (t, C-9), 23.00 (t, C-10), 14.13 (q, C-11).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 194 nm (4.55), 192 (4.53), 196 (4.54), 206 (4.27), 212 (4.18), 216 (4.06), 230 (3.58).

IR (film): $\tilde{\nu}$ = 3068 cm^{-1} (w, C-H stretching, aromatic), 3022 (w, C-H stretching, aromatic), 2955-2856 (s, C-H stretching, aliphatic), 1470, 1459 (w), 1275 (w).

MS (EI, 70 eV): *m/z* (%) = 264 [M^+] (46), 265 [M^++1] (7), 266 [M^++2] (3), 236 [M^+-C_2H_4] (100), 169 [M^+-$C_2H_4S_2$] (51), 105 [M^+-$C_{12}H_{16}$] (57), 77 [$C_6H_5^+$] (24).

4.2.2c. Bis-thioacetal of 2-pentylindanone (54c)

Yield = 18 g, 72%

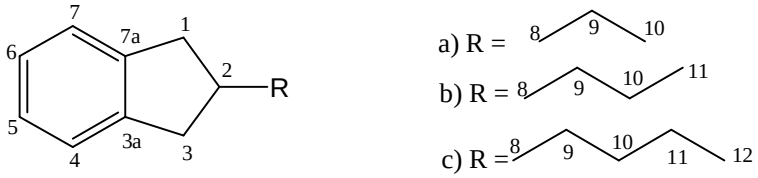
R_F (SiO_2; pentane) = 0.2

B. p. = 220 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 6.0 Hz, 3 H, 12-H), 1.39-1.98 (m, 8 H, side chain protons), 2.56-2.80 (m, 2 H, 3-H), 3.02-3.07 (m, 1 H, 2-H), 3.31-3.61 (m, 4 H, 13 / 13a-H), 7.17-7.30 (m, 4 H, aromatic protons).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.07 (q, C-12), 22.66 (t, C-11), 27.86 (t, C-9), 29.32 (t, C-8), 32.14 (t, C-10), 36.58 (t, C-3), 40.48, 40.93 (2 x t, C-13, C-13a), 54.64 (d, C-2), 124.20 (d, C-7), 124.31 (d, C-4), 127.08 (d, C-8), 127.74 (d, C-5), 140.67 (s, C-7a), 148.41 (s, C-3a).
UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (4.05), 212 (4.05), 258 (2.95), 264 (2.94), 270 (2.95), 278 (2.88), 324 (2.09), 366 (2.00).
IR (film): $\tilde{\nu}$ = 3037, 3022 cm^{-1} (w, C-H stretching, aromatic), 2955, 2925 (s, C-H stretching, aliphatic), 1470, 1459 (m), 1275, 747 (s).
MS (EI, 70 eV): *m/z* (%) = 278 [M^+] (44), 250 [M^+-C_2H_4] (73), 217 [250-SH] (40), 186 [250-S_2] (9), 179 [250-C_5H_{11}] (71), 115 [179-S_2] (76), 103[115-12] (5), 43[C_3H_7] (100).

4.2.3a. 2-Propylindan (53a)



53a-c

A mixture of **54a** (18 g, 0.072 mol) and Raney nickel (100 g) in ethanol (300 mL, 95 %) was refluxed for 8 h. The cooled mixture was filtered and the filtrate diluted with water (100 mL), extracted with ether (2 x 100 mL) and the combined ether extracts were washed with water. The dried (Na_2SO_4) extract was concentrated and purified after passing through a small column of silica gel to get 78 % of 2-propylindan (**53a**) as a colourless liquid.

R_F (SiO_2; pentane) = 0.7
B. p. = 85-90 °C / 1 torr (Lit.[51] 85-90 °C / 1 torr)
^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.04 (t, ^3J = 7.07 Hz, 3 H, 10-H), 1.43-1.61 (m, 5 H, side chain protons, 2-H), 2.50-3.18 (m, 4 H, 1 / 3-H), 7.17-7.29 (m, 4 H, aromatic ring protons).
^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.3 (q, C-10), 21.57 (t, C-9), 38.14 (t, C-3), 39.40 (2 x t, C-1 / 3), 40.07 (d, C-8), 124.40 (2 x d, C-5 / 6), 126.02 (2 x d, C-4 / 7), 143.73 (2 x s, C-3a / 7a).
IR (film): $\tilde{\nu}$ = 2956 cm^{-1}(s, CH-stretching, aliphatic), 2928 (s, C-H stretching, aliphatic), (3043, 3022 (m, CH-stretching, aromatic), 1378 (m, CH_3-deformation), 1601 (s, C=C aromatic).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 194 nm (4.50), 196 (4.50), 198 (4.42), 202 (3.97), 204 (3.85), 208 (3.80), 216 (3.73), 264 (2.75), 268 (2.93), 274 (2.96).

MS (EI, 70 eV): *m/z* (%) = 160 [M^+](67), 131 [M^+-C_2H_5](64), 117 [M^+-C_3H_7](100), 104 [117-CH](63).

HRMS ($C_{12}H_{16}$): Calcd. 160.1252; found 160.1245 ± 2 ppm

4.2.3b. 2-Butylindan (53b)

Yield = 10 g, 85 %

R_F (SiO_2; pentane) = 0.79

B. p. = 120 °C / 14 torr (Lit.[49b, c] 120 °C / 14 torr)

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.98 (t, ^3J = 6.92 Hz, 3 H, 11-H), 1.37-1.59 (m, 6 H, side chain protons), 2.44-2.50 (m, 1 H, 2-H), 2.60-3.12 (m, 4 H, 1 / 3-H), 7.15-7.35 (m, 4 H, aromatic protons).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.13 (q, C-11), 22.87 (t, C-10), 30.65 (t, C-9), 35.51 (t, C-8), 39.36 (2 x t, C-1 / 3), 40.24 (d, C-2), 124.34 (2 x d, C-5 / 6), 125.94 (2 x d, C-4 / 7), 143.70 (2 x s, C-3a, C-7a).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (4.59), 194 (4.57), 198 (4.54), 204 (3.99), 208 (3.90), 216 (3.84), 220 (3.63), 224 (3.17), 268 (3.05), 274 (3.06).

IR (film): $\tilde{\nu}$ = 3096, cm^{-1} (w, C-H stretching, aromatic), 3022 (w, C-H stretching, aromatic), 2956, 2852 (s, C-H stretching, aliphatic), 1459, 1482 (w).

MS (EI, 70 eV): *m/z* (%) = 174 [M^+] (73), 117 [M^+-C_4H_9] (100), 131 [M^+-C_3H_7] (51), 104 [M^+-C_5H_{10}] (78), 91 [$C_7H_7^+$] (35), 77 [$C_6H_5^+$] (13).

4.2.3c. 2-Pentylindan (53c)

Yield = 10 g, 89%

R_F (SiO_2; (pentan) = 0.9

B. p. = 134 °C / 14 torr (Lit.[49c] 134 °C / 14 torr)

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.95 (t, ^3J = 6.6 Hz, 3 H, 12-H), 1.31-1.56 (m, 9 H, side chain protons, 2-H), 2.56-3.13 (m, 4 H, 1 /3-H), 7.13-7.25 (m, 4 H, aromatic protons).

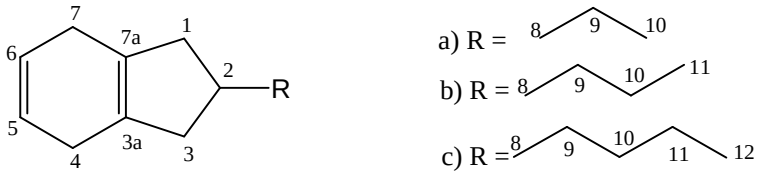
^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.10 (q, C-12), 22.71 (t, C-11), 28.12 (t, C-9), 32.07 (t, C-8), 35.82 (t, C-10), 39.39 (2 x t, C-1 / 3), 40.29 (d, C-2), 124.35 (2 x d, C-4 / 7), 125.96 (2 x d, C-5 / 6), 143.69 (2 x s, C-3a / 7a).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (4.13), 214 (3.78), 268 (2.93), 274 (2.94), 324 (2.25), 346 (2.21), 374 (2.16).

IR (film): $\tilde{\nu}$ = 3071 cm^{-1} (w, C-H stretching, aromatic), 3044 (w, C-H stretching aromatic), 2956, 2924 (s, C-H stretching, aliphatic), 1482, 1459 (w), 739 (s).

MS (EI, 70 eV): *m/z* (%) = 188.1 [M^+] (88), 173 [M^+-CH_3] (1), 159 [M^+-C_2H_5] (1), 145 [M^+-C_3H_7] (6), 131 [M^+-C_4H_9] (50), 117 [M^+-C_5H_{11}] (100), 104 [117-CH] (60).

4.2.4a. 4,7-Dihydro-2-propylindan (56a)



56a-c

2-Propylindan **53a** (14.5 g, 90.62 mmol), liquid NH_3 (87 mL), EtOH (100 mL) and THF (60 mL, dry) were placed in a 500 mL three-necked flask equipped with a mechanical stirrer and the temperature maintained at –75 °C with a methanol-liquid nitrogen bath. Sodium metal was added until the blue colour persisted for 20 min. The NH_3 was allowed to evaporate overnight. The remaining residue was partitioned between ether and water. The ether layer was evaporated and the resulting liquid was again partitioned between ether and water. The ether layer was dried with $MgSO_4$ and the solvent evaporated to give crude 4,7-dihydro-2-propylindan (**56a**) (13.55 g, 92.3 %) as a colourless liquid. The product was rather unstable and on standing slowly re-oxidized to 2-propylindan, it was thus quickly used for further reaction.

R_F (SiO_2; pentane) = 0.8

B. p. = 52-54 °C / 7 torr

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 7.0 Hz, 3 H, 10-H), 1.28-1.41 (m, 5 H, side chain protons, 2-H), 1.87-2.40 (m, 4 H, 1 / 3-H), 2.61 (br. s, 4 H, 4 / 7-H), 5.74 (br. s, 2 H, 5 / 6-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.25 (q, C-10), 21.37 (t, C-9), 27.51 (2 x t, C-4 / 7), 35.9 (d, C-2), 39.28 (t, C-8), 42.13 (2 x t, C-1 / 3), 124.73 (2 x d, C-5 / 6), 130.92 (s, C-3a / 7a).

IR (film): $\tilde{\nu}$ = 3026 cm^{-1}(m, C-H stretching), 2956, 2915, 2874 (s, CH-stretching), 1377 (m, CH_3-deformation).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (3.88), 194 (3.88), 208 (3.56), 224 (2.98), 230 (2.70), 240 (2.13), 274 (1.94), 296 (1.97).

MS (GC/MS): *m/z* (%) = 162 [M^+] (95), 119 [M^+-C_3H_7] (81), 92 [C_7H_8] (100), 91 (95), 79 (22).

4.2.4b. 4,7-Dihydro-2-butylindan (56b)

Yield = 12 g, 85 %

R_F (SiO_2; pentane) = 0.94

B. p. = 78 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.94 (t, ^3J = 6.84 Hz, 3 H, 11-H), 1.31-1.47 (m, 7 H, side chain protons, 2-H), 1.95-2.47 (m, 4 H, 1 / 3-H), 2.66 (br. s, 4 H, 4 / 7-H), 5.79 (s, 2 H, 5 / 6-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.16 (q, C-11), 22.90 (t, C-10), 27.54 (2 x t, C-1 / 3), 30.62 (t, C-9), 36.19 (t, C-2), 36.72 (d, C-8), 42.20 (2 x t, C-4 / 7), 124.75 (2 x d, C-5 / 6), 130.96 (s, C-3a / 7a).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 194 nm (3.96), 200 (3.83), 208 (3.52), 218 (3.25), 228 (2.68), 268 (2.21), 274 (2.22).

IR (film): $\tilde{\nu}$ = 3026 cm^{-1} (s, C-H-stretching), 2957, 2721 (s), 1466, 1428 (w), 1644 (w), 926, 955 (w).

MS (EI, 70 eV): *m/z* (%) = 176 [M^+] (67), 174 [M^+-H_2] (30), 119 [M^+-C_4H_9] (78), 92 [$C_7H_8^+$] (100).

4.2.4c. 4,7-Dihydro-2-pentylindan (56c)

Yield = 14 g, 97%

R_F (SiO_2; (pentan) = 0.9

B. p.= 138 °C / 2 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.9 (t, ^3J = 6.8 Hz, 3 H, 12-H), 1.29-1.43 (m, 9 H, side chain protons, 2-H), 1.94-2.44 (m, 4 H, 1 / 3-H), 2.66 (br. s, 4 H, 4 / 7-H), 5.78 (s, 2 H, 5 / 6-H).

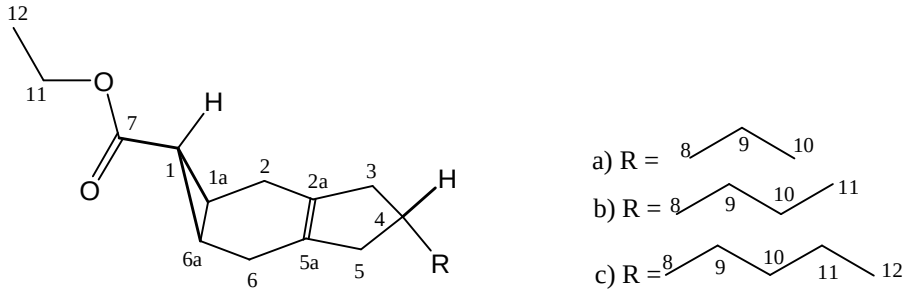
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.09 (q, C-12), 22.71 (t, C-11), 27.55 (2 x t, C-1, C-3), 28.05 (t, C-9), 32.10 (t, C-8), 37.0 (t, C-10), 36.24 (d, C-2), 42.21 (2 x t, C-4, C-7), 124.76 (2 x d, C-5, C-6), 130.96 (s, C-3a, C-7a).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (3.78), 212 (3.46), 252 (1.65), 266 (1.70), 324 (2.33), 360 (2.27).

IR (film): $\tilde{\nu}$ = 3026 cm^{-1} (m, CH-stretching), 2956, 2922, 2873, 2851 (s, C-H stretching), 1645, 1465, 1459, 1443 (w), 661 (m).

MS (EI, 70 eV): *m/z* (%) = 190.1 [M^+] (66), 175 [M^+-CH_3] (1), 161 [M^+-C_2H_5] (1.7), 147 [M^+-C_3H_7] (3), 133 [M^+-C_4H_9] (9.4), 119 [M^+-C_5H_{11}] (100), 105 [119.1-CH_2] (13), 92 [119.1-C_2H_3] (97), 91 [119-C_2H_4] (88).

4.2.5a. 4-Propyl-1,1a,2,3,4,5,6,6a-octahydro-cyclopropa[*f*]indene-1-carboxylic acid ethyl ester (33a)



33a-c

To a refluxing suspension of 4,7-dihydro-2-propylindan (**56a**,14.5 g, 89.50 mmol), $CuSO_4$ (anhydrous, 7.5 g) and cyclohexane (anhydrous, 70 mL) was added dropwise with stirring over a 5 h period, a solution of ethyl diazoacetate (34.69 g, 304.0 mmol) in 150 mL of anhydrous cyclohexane with a dropping funnel. The mixture was refluxed for further 60 min and filtered to remove the $CuSO_4$. The solution was concentrated and the product was separated by column chromatography on silica gel using pentane as solvent increasing its polarity with dichloromethane. Some unreacted starting material eluted from the column first followed by the product (**33a**, 12 g, 54 %) and finally by diethyl fumerate produced as a side product. The small impurities which eluted with the product were further separated with the help of a silver nitrate impregnated silica gel column with pentane as an eluent, increasing its polarity with dichloromethane. An aqueous solution of 5.5 g of silver nitrate in 30 ml of distilled water was mixed with 50 g of 200-300-mesh silica and ground for 5 min in a mortar. The mixture was then dried in an oven at 150 °C for 1 h. The resulting powder was almost white, stored in a beaker wrapped with dark paper and dried over phosphorous pentoxide in a vacuum desiccator. The adsorbent could be stored for several months without significant darkening or decrease of activity. The column was packed in the same way as an ordinary

silica gel column but was wrapped with dark paper. The adduct was a colourless liquid which on keeping below room temperature solidified.

R_F (SiO_2; pentane/CH_2Cl_2; 8:2) = 0.4

M. p. = 15 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 7.0 Hz, 3 H, 10-H), 1.27 (t, ^3J = 7.15 Hz, 3 H, 12-H), 1.25-1.35 (m, 6 H, 8 / 9-H, 1a / 6a-H), 1.45 (t, ^3J = 4.33 Hz, 1 H, 1-H), 1.76-1.81 (br. s, 4 H, 2 / 6-H), 2.14-2.23 (m, 1 H, 4-H), 2.31 (br. s, 4 H, 3 / 5-H), 4.12-4.14 (q, ^3J = 7.1 Hz, 2 H, 11-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.50, 14.56 (2 x q, C-10 / 12), 21.60 (t, C-9), 22.49 (2 x d, C-1a / 6a), 24.41 (d, C-4), 24.46 (2 x t, C-2 / 6), 36.23 (d, C-1), 39.36 (t, C-8), 42.71 (2 x t, C-3 / 5), 60.44 (t, C-11), 129.26 (2 x s, C-2a / 5a), 175.30 (s, C-7).

IR (film): $\tilde{\nu}$ = 2956 cm^{-1} (m, CH-stretching), 1724 (s, C=O), 1376 (m, CH_3-deformation), 1213, 1172 (s, C-O).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (3.93), 238 (1.30), 268 (1.28), 282 (0.89), 296 (1.31), 380 (1.31).

MS (EI, 70 eV): *m/z* (%) = 248 [M^+] (100), 220 [M^+-CO] (5), 219 [M^+-C_2H_5] (22), 203 [M^+-C_2H_5O] (30), 194 (20), 175 [M^+-$C_3H_5O_2$] (33), 162 [175-CH] (72), 131 (53), 112 (90), 105 (32).

Elemental analysis $C_{16}H_{24}O_2$ (248.8): Calcd. C 77.36 %, H 9.75 %; found C 76.92 %, H 10.11 %.

4.2.5b. 4-Butyl-1,1a,2,3,4,5,6,6a-octahydro-cyclopropa[*f*]indene-1-carboxylic acid ethyl ester (33b)

Yield = 13 g, 63 %

R_F (SiO_2; pentane: Ether; 9:1) = 0.76

M. p. = melts at room temperature

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.79 (t, ^3J = 7.01 Hz, 3 H, 11-H), 1.18 (t, ^3J = 7.13 Hz, 3 H, 13-H), 1.10-1.31 (m, 8 H, side chain protons, 1a / 6a-H), 1.23 (t, ^3J = 4.87 Hz, 1 H, 1-H), 1.47-1.74 (m, 4 H, 2 / 6-H), 2.05-2.10 (m, 1 H, 4-H), 2.23 (br. s, 4 H, 3 / 5-H), 4.03 (q, ^3J = 7.12 Hz, 2 H, 12-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.09 (q, C-11), 14.26 (q, C-13), 22.19 (2 x d, C-1a, C-6a), 22.81 (t, C-10), 26.12 (d, C-4), 30.05 (2 x t, C-2 / 6), 30.49 (t, C-9), 36.15 (d, C-1), 36.47 (t, C-8), 42.45 (2 x t, C-3 / 5), 60.16 (t, C-12), 128.96 (2 x s, C-2a / 5a), 174.99 (s, C-7).

UV/Vis (CH_3CN): λ_{max} (lg ε) =192 nm (3.93), 204 (3.69), 216 (3.23), 228 (2.70), 240 (2.31), 294 (2.21), 342 (2.16).

IR (film): $\tilde{\nu}$ = 3025 cm^{-1} (w), 2977, 2722 (s, CH-stretching), 1445, 1465 (w), 1725 (s, C=O), 1172, 1287 (s).

MS (EI, 70 eV): *m/z* (%) = 262 [M^+] (88), 233 [M^+-C_2H_5] (18), 217 [M^+-C_2H_5O] (28), 149 [M^+-$C_6H_9O_2$] (12), 112 [M^+-$C_{11}H_{18}$] (100).

4.2.5c. 4-Pentyl-1, 1a, 2, 3, 4, 5, 6, 6a-octahydro-cyclopropa[*f*]indene-1-carboxylic acid ethyl ester (33c)

Yield = 13.5 g, 64 %

R_F (SiO_2; (pentan : dichloromethane; 8 : 2) = 0.3

M. p. = above 5 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.91 (t, ^3J = 6.8 Hz, 3 H, 12-H), 1.28 (t, ^3J = 7.1 Hz, 3 H, 14-H), 1.24-1.42 (m, 10 H, side chain protons, 1a / 6a-H), 1.46 (t, ^3J = 4.27 Hz, 1 H, 1-H), 1.70-1.92 (m, 4 H, 2 / 6-H), 2.20-2.24 (m, 1 H, 4-H), 2.32 (br. s, 4 H, 3 / 5-H), 4.15 (q, ^3J = 7.2 Hz, 2 H, 13-H).

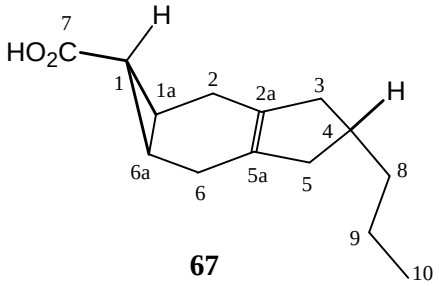
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.37 (q, C-12), 14.60 (q, C-14), 22.54 (2 x d, C-1a / 6a), 22.97 (t, C-11), 23.65 (d, C-1), 24.50 (2 x t, C-2 / 6), 28.25 (t, C-10), 32.33 (t, C-9), 36.52 (d, C-4), 37.28 (t, C-8), 42.79 (2 x t, C-3 / 5), 60.49 (t, C-13), 129.30 (2 x s, C-2a / 5a), 175.7 (s, C=O).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 198 nm (3.66), 214 (4.13), 324 (2.67), 350 (2.62).

IR (film): $\tilde{\nu}$ = 2982 cm^{-1} (s, C-H stretching aliphatic), 1724 (s, C=O), 1465, 1445, 1368 (m), 1297, 1260, 1224 (s), 1173, 1155 (s), 1142, 1037 (s).

MS (EI, 70 eV): *m/z* (%) = 276 [M^+] (51), 247 [M^+-C_2H_5] (18), 231 [M^+-C_2H_5O] (18), 203 [M^+-$C_2H_5CO_2$] (25), 188 [203-CH_3] (35), 205 [M^+-C_5H_{11}] (16), 159 [205-C_2H_6O] (20), 131 [159-CO] (70), 117 [131-CH_2] (35), 112 [$C_6H_8O_2$] (100), 105 [131-C_2H_2] (38), 91 [105-CH_2] (58).

4.2.6a. 4-Propyl-1,1a,2,3,4,5,6,6a-octahydro-cyclopropa[*f*]indene-1-carboxylic acid (67)



67

In a 100 mL round-bottomed flask 100 mL of EtOH and 60 mL of 1M NaOH were placed. The mixture was left to stir for a while and the ethyl ester **33a** (2.0 g, 8.064 mmol) was added slowly; the mixture was kept at room temperature and stirred for 4-6 h. When TLC analysis showed no more starting material to be present, the mixture was acidified with 1M HCl. The EtOH was evaporated and the residual water extracted twice with ethyl acetate and once with CH_2Cl_2. The organic parts were combined, washed with water and dried ($MgSO_4$). The solvent was evaporated and the residue purified by column chromatography on silica gel by first eluting the impurities with CH_2Cl_2 and finally washing the column with Et_2O to yield 1.5 g (84 %) of the compound as a colourless solid which was recrystallized from hexane/dichloromethane to yield analytically pure cubes.

R_F (SiO_2; dichloromethane) = 0.17

M. p. = 80-83 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.0 Hz, 3 H, 10-H), 1.27-1.37 (m, 6 H, 8 / 9-H, 1a / 6a-H), 1.47 (t, ^3J = 4.2 Hz, 1 H, 1-H), 1.85-1.89 (br. s, 4 H, 2 / 6-H), 2.25 (m, 1 H, 4-H), 2.33 (br. s, 4 H, 3 / 5-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.22 (q, C-10), 21.30 (t, C-9), 23.31 (d, C-4), 23.34 (2 x d, C-1a / 6a), 24.14 (2 x t, C-2 / 6), 35.91 (d, C-1), 39.08 (t, C-8), 42.38 (2 x t, C-3 / 5), 128.89 (2 x s, C-2a / 5a), 181.63 (s, C-7).

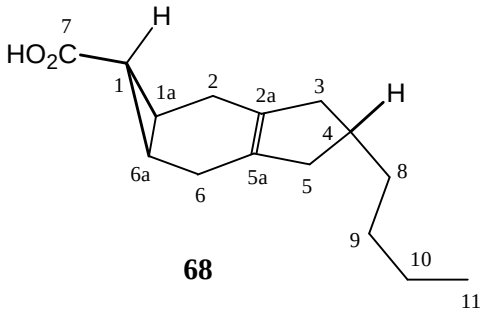
UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (4.00).

IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1} (s, C-H stretching), 2877, 2835 (m), 2674, 2624, 2580 (w), 1686 (s, C=O), 1466, 1452, 1434, 1347 (m), 1303, 1217 (m), 1013 (w).

MS (EI, 70 eV): *m/z* (%) = 220 [M^+] (53), 202 [M^+-H_2O] (11), 177 [M^+-C_3H_7] (30), 160 [177-OH] (41), 131 [177-HCOOH] (75), 105 [C_8H_9] (55), 91 [105-CH_2] (100).

Elemental analysis $C_{14}H_{20}O_2$ (220.31): Calcd. C 76.33 %, H 9.15 %, O 14.52 %; found C 76.31 %, H 9.18 %.

4.2.6b. 4-Butyl-1,1a,2,3,4,5,6,6a-octahydro-cyclopropa[*f*]indene-1-carboxylic acid (68)



68

Yield = 1.5 g, 85 %

R_F (SiO_2; dichloromethane) = 0.2

M. p. = 78-80 °C (recrystallized from hexane/dichloromethane to get colourless needles).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 6.9 Hz, 3 H, 11-H), 1.25-1.38 (m, 8 H, side chain protons, 1a / 6a-H), 1.43 (t, ^3J = 4.24 Hz, 1 H, 1-H), 1.85 (br. s, 4 H, 2 / 6-H), 2.16-2.25 (m, 1 H, 4-H), 2.34 (br. s, 4 H, 3 / 5-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.12 (q, C-11), 22.83 (t, C-10), 23.29 (d, C-4), 23.35 (2 x d, C-1a / 6a), 24.15 (2 x t, C-3 / 5), 30.50 (t, C-9), 36.14 (d, C-1), 36.49 (t, C-8), 42.43 (2 x t, C-2 / 6), 128.89 (2 x s, C-2a / 5a), 181.58 (s, C-7).

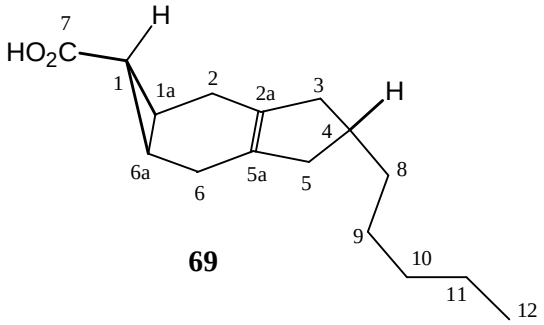
UV/Vis (CH_3CN): λ_{max} (lg ε) = 198 nm (4.18), 202 (4.15), 206 (4.13), 244 (2.29), 254 (2.47).

IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1} (s, C-H stretching), 1686 (s, C=O), 1655, 1648 (w), 1466, 1458, 1445 (m), 1344 (w), 1299, 1213(m).

MS (EI, 70 eV): *m/z* (%) = 234 [M^+] (55), 216 [M^+-H_2O] (9), 205 [M^+-C_2H_5] (5), 189 [M^+-CO_2H] (21), 177 [M^+-C_4H_9] (69), 159 [177-H_2O] (29), 131 [177-HCOOH] (85), 117 [131-CH_2] (66), 105 [C_8H_9] (66), 91 [131-C_3H_4] (100).

Elemental analysis $C_{15}H_{22}O_2$ (234.34): Calcd. C 77.21 %, H 9.07 %, O 13.71 %; found C 77.56 %, H 9.10 %.

4.2.6c. 4-Pentyl-1,1a,2,3,4,5,6,6a-octahydro-cyclopropa[*f*]indene-1-carboxylic acid (69)



69

Yield = 1.4 g, 80 %

R_F (SiO_2; dichloromethane = 0.2

M. p. = 72-74 °C (recrystallized from hexane/dichloromethane to colourless irregular crystals).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.80 (t, ^3J = 6.8 Hz, 3 H, 12-H), 1.13-1.31 (m, 10 H, side chain protons, 1a /6a-H), 1.37 (t, ^3J = 4.23 Hz, 1 H, 1-H), 1.74 (br. s, 4 H, 2 / 6-H), 2.05-2.14 (m, 1 H, 4-H), 2.23 (br. s, 4 H, 3 / 5-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.07 (q, C-12), 22.67 (t, C-11), 23.20 (d, C-1), 23.34 (2 x d, C-1a / 6a), 24.16 (2 x t, C-3 / 5), 27.92 (t, C-10), 32.02 (t, C-9), 36.18 (d, C-4), 36.77 (t, C-8), 42.44 (2 x t, C-2 / 6), 128.90 (2 x s, C-2a / 5a), 181.05 (s, C=O).

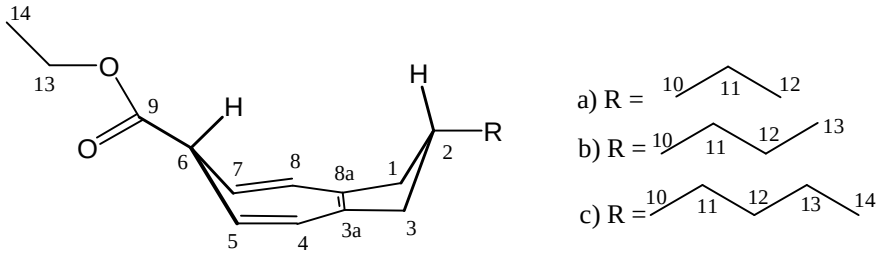
UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (4.05), 212 (3.95), 244 (3.08), 250 (3.02), 258 (2.95), 324 (2.65), 354 (2.60), 374 (2.57).

IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (s, C-H stretching), 1690 (s, C=O), 1686 (s), 1448 (m), 1384 (m), 1298 (m), 1209 (m).

MS (EI, 70 eV): *m/z* (%) = 249 [M^++1] (13), 248 [M^+] (91), 230 [M^+-H_2O] (8), 201 [230-C_2H_5] (20), 188 [201-CH] (28), 177 [M^+-C_5H_{11}] (67), 131 [177-HCOOH] (87), 117 [131-CH_2] (55), 105 [131-C_2H_2] (59), 91 [131-C_3H_4] (100).

Elemental analysis $C_{16}H_{24}O_2$ (248.37): Calcd. C 77.38 %, H 9.74 %; found C 77.45 %, H 9.87 %.

4.2.7a. Ethyl 2-propyl-1,2,3,6-tetrahydro-6-azulenecarboxylate (59a)



59a-c

4-Propyl-1,1a,2,3,4,5,6,6a-octahydro-cyclopropa[*f*]indene-1-carboxylic acid ethyl ester **33a** (8 g, 32.25 mmol) was dissolved in CCl_4 (400 mL) and the solution cooled with an ice bath. Bromine (5.155 g, 32.25 mmol) dissolved in CCl_4 (18 mL) was added dropwise with stirring. When the addition was complete, triethylamine, 16 g (158.11 mmol) was added. Triethylamine hydrobromide began to form immediately. The mixture was refluxed for 18 h. After cooling, the HBr salt was filtered off. The filtrate was evaporated and the resulting oil partitioned between benzene and dilute aqueous acid (HCl). The benzene layer was washed with water and dried with $MgSO_4$ and filtered to get the crude product. The product was purified by column chromatography on silica gel using pentane as solvent and increasing the polarity with dichloromethane. The product (**59a**, 5.5 g, 69.3 %) which was a clear bluish liquid, eluted with 1% dichloromethane.

R_F (SiO_2; pentane/diethyl ether; 9:1) = 0.5

B. p. = 124-126 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.2 Hz, 3 H, 12-H), 1.30 (t, ^3J = 7.14 Hz, 3 H, 14-H), 1.33-1.37 (m, 4 H, 10 / 11-H), 2.34 (m, 1 H, 2-H), 2.38-2.41 / 2.79-2.85 (m, 4 H, 1 / 3-H), 2.67-2.71 (m, 1 H, 6-H), 4.22-4.27 (q, ^3J = 7.14 Hz, 2 H, 13-H), 5.34-5.41 (m, 2 H, 5 / 7-H), 6.17-6.21 (2 x d, ^3J = 9.1 Hz, 2 H, 4 / 8-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.23 (2 x q, C-12, C-14), 21.39 (t, C-11), 37.06 (d, C-2), 38.20 (t, C-10), 42.75 (2 x t, C-1 / 3), 45.20(d, C-6), 60.93 (t, C-13), 115.99, 116.63 (2 x d, C-5 / 7), 125.29, 125.44 (2 x d, C-4 / 8), 141.81 (s, C-3a / 8a), 173.27 (s, C-9).

IR (film): $\tilde{\nu}$ = 2958 cm^{-1}(m, CH-stretching), 1738 (s, C=O), 1610 (w), 1465, 1447 (w), 1392 (w), 1368, 1301, 1292, 1274 (m), 1255, 1193, 1179, 1164 (m), 1105, 1069 (w).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 228 nm (3.77), 236 (3.68), 246 (3.66), 264 (3.50), 288 (3.44), 300 (3.31), 318 (3.02).

MS (EI, 70 eV): *m/z* (%) = 246 [M^+] (10), 217 [M^+-C_2H_5] (10), 218 [M^+-CO] (4), 173 [M^+-$C_3H_5O_2$] (100), 129 [173-C_3H_8] (7).

4.2.7b. Ethyl 2-butyl-1,2,3,6-tetrahydro-6-azulenecarboxylate (59b)

Yield = 5.2 g, 66 %

R_F (SiO_2; pentane/ether; 9:1) = 0.56

B. p. = 135 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.1 Hz, 3 H, 13-H), 1.34 (t, ^3J = 7.16 Hz, 3 H, 15-H), 1.37-1.51 (m, 6 H, side chain protons), 2.19-2.21 (m, 1 H, 2-H), 2.37-2.43 / 2.85-2.88 (m, 4 H, 1 / 3-H), 2.72-2.83 (m, 1 H, 6-H), 4.16 (q, ^3J = 7.132 Hz, 2 H, 14-H), 5.38-5.45 (m, 2 H, 5 / 7-H), 6.21-6.24 (2 x d, ^3J = 9.02 Hz, 2 H, 4 / 8-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.08 (q, C-13), 14.20 (q, C-15), 22.81 (t, C-12), 30.53 (t, C-11), 35.62 (t, C-10), 37.27 (d, C-2), 42.78 (2 x t, C-1 / 3), 45.18 (d, C-6), 60.89 (t, C-14), 116.60 (2 x d, C-5 / 7), 125.41 (2 x d, C-4 / 8), 141.77 (s, C-3a / 8a), 173.24 (s, C-9).

UV/VIS (CH_3CN): λ_{max} (lg ε) = 206 nm (4.31), 208 (4.30), 254 (3.50), 268 (3.57), 292 (3.38), 310 (3.01), 342 (2.39).

IR (film): $\tilde{\nu}$ = 3024 cm^{-1} (w), 2957, 2852 cm^{-1} (s, CH-stretching), 1466, 1447 (w) 1739 (s, C=O), 1193, 1259 (s, C-O).

MS (EI, 70 eV): *m/z* (%) = 260 [M^+] (13), 231 [M^+-C_2H_5] (6), 232 [M^+-CO] (1), 87 [M^+-$C_3H_5O_2$] (100), 129 [187-C_4H_{10}] (8), 88 [129-C_3H_5] (16).

4.2.7c. Ethyl 2-pentyl-1,2,3,6-tetrahydro-6-azulenecarboxylate (59c)

Yield = 6.2 g, 79%

R_F (SiO_2; (pentan/dichloromethane; 8 : 2) = 0.3

B. p. = > 260 °C / 2 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.0 Hz, 3 H, 14-H), 1.29-1.34 (t, ^3J = 7.1 Hz, 3 H, 16-H), 1.31-1.38 (m, 8 H, side chain protons), 1.62-1.74 / 2.42-2.47 (m, 4 H, 1-H, 3-H), 2.38-2.41 (m, 1 H, 2-H), 2.83 (m, 1 H, 6-H), 4.30 (q, ^3J = 7.1 Hz, 2 H, 15-H), 5.41-5.45 (m, 2 H, 5 / 7-H), 6.21 (2 x d, ^3J = 9.10 Hz, 2 H, 4 / 8-H).

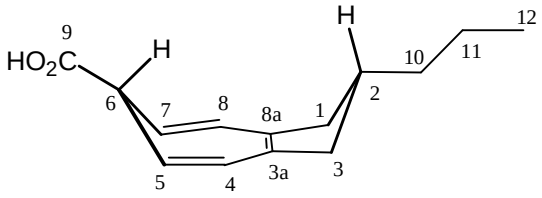
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.07 (q, C-14), 14.24 (q, C-16), 22.66 (t, C-13), 26.02 (t, C-12), 33.01 (t, C-11), 35.92 (t, C-10), 37.32 (d, C-2), 42.80 (2 x t, C-1 / 3), 45.20 (d, C-6), 60.93 (t, C-15), 115.97, 116.63 (2 x d, C-5 / 7), 125.30, 125.45 (2 x d, C-4 / 8), 141.81 (s, C-3a / 8a), 173.28 (s, C-9).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 206 nm (4.14), 274 (3.64), 288 (3.64), 312 (3.50), 344 (3.30), 374 (2.98).

IR (film): $\tilde{\nu}$ = 3023 cm^{-1} (w, C-H stretching), 2956, 2925 (s, C-H stretching aliphatic), 1737 (s, C=O), 1465, 1447, 1367, 1301 (w), 1256 (m), 1223 (w), 1192, 1175, 1161 (m).

MS (EI, 70 eV): *m/z* (%) = 274 [M^+] (5), 245 [M^+-C_2H_5] (5), 228 [245-OH] (2), 201 [M^+-$C_3H_5O_2$] (100), 129 [201-C_5H_{12}] (10).

4.2.8a. 2-Propyl-1,2,3,6-tetrahydro-azulene-6-carboxylic acid (70)



70

The procedure for the hydrolysis of the ethyl ester **59a** of the above acid was the same as described before for **67**. The acid was recrystallized from hexane/dichloromethane mixture to yield colourless irregular crystals.

Yield = 0.5 g, 81 %

R_F (SiO_2; dichloromethane) = 0.2

M. p. = 118-120 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.1 Hz, 3 H, 12-H), 1.36-1.50 (m, 4 H, side chain protons), 2.29 (m, 1 H, 2-H), 2.39-2.44 / 2.82-2.88 (m, 4 H, 1 / 3-H), 2.89-2.90 (m, 1 H, 6-H), 5.43-5.46 (dd, $^3J_{5,4}$ = $^3J_{7,8}$ = 9.07Hz, $^3J_{5,6}$ = $^3J_{7,6}$ = 5.6Hz, 2 H, 5 / 7-H), 6.24-6.27 (2 x d, ^3J = 9.1Hz, 2 H, 4 / 8-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.23 (q, C-12), 21.39 (t, C-11), 37.04 (d, C-2), 38.18 (t, C-10), 42.75 (2 x t, C-1, C-3), 44.72 (d, C-6), 115.74 (2 x d, C-5, C-7), 125.81 (2 x d, C-4, C-8), 141.95 (2 x s, C-3a, C-8a), 178.20 (s, C=O).

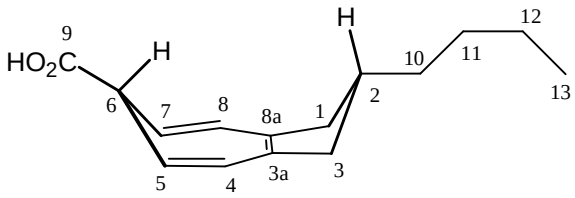
UV/Vis (CH_3CN): λ_{max} (lg ε) = 206 nm (4.31), 268 (3.57).

IR (KBr): $\tilde{\nu}$ = 3023 cm^{-1} (w, C-H stretching), 2964, 2950, 2924 (m, C-H stretching), 2834, 2871, 2829 (w), 2700 (w), 2596 (w), 1713 (s, C=O), 1686 (w), 1655 (w), 1419(w), 1312, 1298, 1220 (w).

MS (EI, 70 eV): *m/z* (%) = 218 [M^+] (14), 200 [M^+-H_2O] (6), 173 [M^+-CO_2H] (100), 129 [173-C_3H_8] (17).

Elemental analysis $C_{14}H_{18}O_2$ (218.30): Calcd. C 77.02 %, H 8.32 %; found C 77.08 %, H 8.17 %.

4.2.8b. 2-Butyl-1,2,3,6-tetrahydro-azulene-6-carboxylic acid (71)



71

Yield = 0.49 g, 78 %

R_F (SiO_2; dichloromethane) = 0.2

M. p. = 78-81 °C (Compound was obtained as a light brownish coloured solid).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.94 (t, ^3J = 6.86 Hz, 3 H, 13-H), 1.30-1.39 (m, 6 H, side chain protons), 1.40-1.55 (m, 4 H, 1 / 3-H), 2.27-2.30 (m, 1 H, 2-H), 2.83-2.87 (m, 1 H, 6-H), 5.39-5.43 (dd, $^3J_{5,4}$ = $^3J_{7,8}$ = 9.0Hz, $^3J_{5,6}$ = $^3J_{7,6}$ = 5.7Hz, 2 H, 5 / 7-H), 6.24-6.27 (d, ^3J = 9.1Hz, 2 H, 4 / 8-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.11 (q, C-13), 22.82 (t, C-12), 30.54 (t, C-11), 35.82 (t, C-10), 37.79 (d, C-2), 42.98 (2 x t, C-1 / 3), 44.71 (d, C-6), 115.73 (2 x d, C-5 / 7), 125.62 (2 x d, C-4 / 8), 141.82 (2 x s, C-3a / 8a), 179.20 (s, C-9).

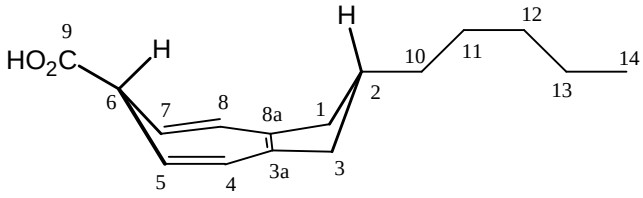
UV/Vis (CH_3CN): λ_{max} (lg ε) = 206 nm (4.31), 248 (3.56), 268 (3.47), 300 (3.04).

IR (KBr): $\tilde{\nu}$ = 3024 cm^{-1} (w, C-H stretching), 2956, 2924, 2872, 2853 (s, C-H stretching), 2695, 2596 (w), 1710 (s, C=O), 1612, 1466, 1455 (w), 1420, 1298 (m), 1211 (w).

MS (EI, 70 eV): *m/z* (%) = 232 [M^+] (15), 214 [M^+-H_2O] (8), 187 [M^+-CO_2H] (100), 129 [187-C_4H_{10}] (21).

No elemental analysis was determined because of scarcity of material.

4.2.8c. 2-Pentyl-1,2,3,6-tetrahydro-azulene-6-carboxylic acid (72)



72

Yield = 0.5 g, 82 %

R_F (SiO_2; dichloromethane) = 0.2

M. p. = 70-72 °C (recrystallized from hexane / dichloromethane mixture to yield lightly coloured monoclinic crystals).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 5.9Hz, 3 H, 14-H), 1.25-1.50 (m, 8 H, side chain protons), 2.27-2.30 (m, 1 H, 2-H), 2.32-2.84 (m, 4 H, 1 / 3-H), 2.87-2.90 (m, 1 H, 6-H), 5.43-5.46 (dd, $^3J_{5,4}$ = $^3J_{7,8}$ = 9.2Hz, $^3J_{5,6}$ = $^3J_{7,6}$ = 5.7Hz, 2 H, 5-H, 7-H), 6.25-6.28 (d, ^3J = 8.9Hz, 2 H, 4-H, 8-H).

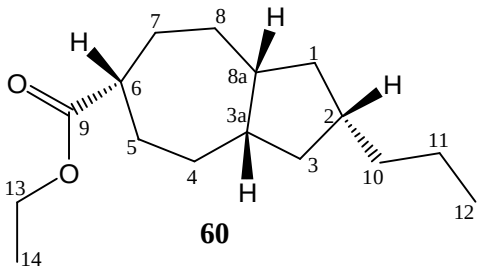
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.07 (q, C-14), 22.67 (t, C-13), 27.98 (t, C-12), 32.0 (t, C-11), 35.90 (t, C-10), 37.30 (d, C-2), 42.98 (2 x t, C-1 / 3), 44.72 (d, C-6), 115.75 (2 x d, C-5 / 7), 125.81 (2 x d, C-4 / 8), 141.95 (2 x s, C-3a / 8a), 178.17 (s, C=O).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 206 nm (4.30), 268 (3.53).

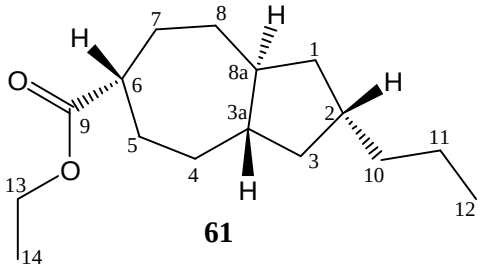
IR (KBr): $\tilde{\nu}$ = 3023 cm^{-1} (w, C-H stretching), 2957, 2923, 2870, 2853 (m, C-H stretching), 2699, 2595 (m), 1712 (s, C=O), 1420, 1312, 1219 (m).

MS (EI, 70 eV): *m/z* (%) = 246 [M^+] (12), 228 [M^+-H_2O] (5), 201 [M^+-CO_2H] (100), 129 [201-C_5H_{12}] (21);

4.2.9a. Ethyl 2-propyl perhydro-6-azulenecarboxylate (60/61)



60



61

Ethyl 2-propyl-1,2,3,6-tetrahydro-6-azulenecarboxylate **59a** (3.29 g, 13.37 mmol) was dissolved in ethyl acetate (300 mL) in a 500 mL flask and Pd/C (1.1 g) added to the mixture.

A stream of H_2 was blown through the suspension after evacuation, and the flask was shaken for 2 h with continuous addition of H_2. The mixture was filtered to remove the catalyst and the solvent was evaporated to yield the product (3.09 g, 91.7 %) as a colourless liquid. The product was obtained in the form of a mixture of isomers, which were later separated by column chromatography on silica gel with pentane. The *cis*-fused isomer (**60**) eluted first followed by the *trans*-diastereomer (**61**). However, pure *trans*-fused material could not be separated as it always contained traces of the *cis*-fused derivative. The spectroscopic data for **60** are given below.

R_F (SiO_2; pentane/ CH_2Cl_2, 7:3) = 0.4

B. p. = 135-140 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 6.94 Hz, 3 H, 12-H), 1.28 (t, ^3J = 7.12 Hz, 3 H, 14-H), 1.30-1.33 (m, 4 H, side chain protons), 1.51-1.53 (m, 2 H, 3a / 8a-H), 1.55-1.60 (m, 4 H, 4 / 8-H), 1.67-1.72 (m, 1 H, 2-H), 0.82 / 1.89 (m, 4 H, 1 / 3-H), 2.10-2.14 (m, 4 H, 5 / 7-H), 2.64-2.67 (m, 1 H, 6-H), 4.15 (q, ^3J = 7.12, 2 H, 13-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.26 (q, C-12), 14.38 (q, C-14), 21.78 (t, C-11), 28.75 (2 x t, C-4 / 8), 29.56 (2 x t, C-5 / 7), 37.79 (t, C-10), 39.94 (d, C-2), 41.63 (2 x t, C-1 / 3), 41.87 (2 x d, C-3a / 8a), 43.41 (d, C-6), 59.97 (t, C-13), 176.11 (s, C=O).

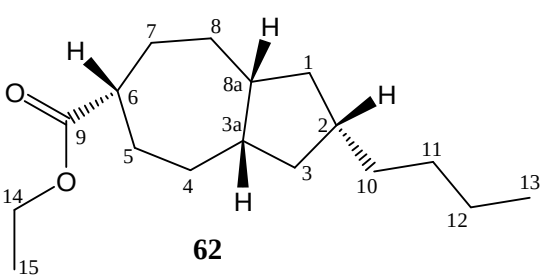
IR (film): $\tilde{\nu}$ = 2932 cm^{-1}(s, CH-stretching), 1732 (s, C=O), 1463, 1450 (w), 1376, 1221 (w), 1183, 1143 (m), 1095, 1046, 1033 (w).

UV / Vis (CH_3CN): λ_{max} (lg ε) = 204 nm (2.92), 216 (2.55), 234 (2.15), 284 (1.86), 312 (1.80), 342 (1.64), 374 (1.54).

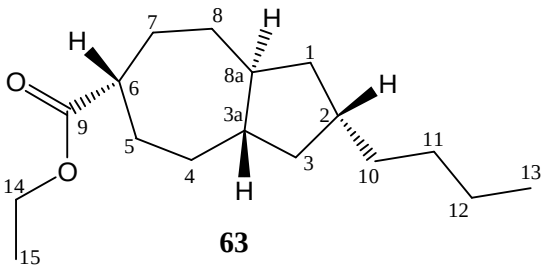
GC/MS (EI, 70 eV): *m/z* (%) = 252 [M^+] (95), 237 [M^+-CH_3] (5), 223 [M^+-C_2H_5] (12), 209 [M^+-C_3H_7] (29), 206 [223-OH] (18), 178 [206-CO] (15), 163 [206-C_3H_7] (100), 135 [163-CO] (57), 109 [135-C_2H_2] (52), 81 [109-C_2H_4] (49).

HRMS ($C_{16}H_{28}O_2$): Calcd.252.2089; found 252.20856 ± 0.5 ppm.

4.2.9b. Ethyl 2-butyl perhydro-6-azulenecarboxylate (62/63)



62



63

The procedure for the hydrogenation of **59b** to get **62/63** was the same as described earlier for **59a** (1.07 g (4.24 mmol) of **59b**; 0.23 g of Pd/C in 100 mL of EtOAc). Product **62/63** obtained as a colourless liquid. The spectroscopic and analytical data for **62** is given below.

Yield = 1.02 g, 90 %

R_F (SiO_2; pentane/CH_2Cl_2; 7:3) = 0.46

B. p. = 146 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 6.74 Hz, 3 H, 13-H), 1.28 (t, ^3J = 7.12 Hz, 3 H, 15-H), 1.27-1.34 (m, 6 H, side chain protons), 1.49-1.53 (m, 2 H, 3a / 8a-H), 1.53-1.59 (m, 4 H, 4 / 8-H), 1.70 (m, 1 H, 2-H), 0.82 / 1.89 (m, 4 H, 1 / 3-H), 2.09-2.16 (m, 4 H, 5 / 7-H), 2.64-2.67 (m, 1 H, 6-H),4.13-4.18 (q, ^3J = 7.12 Hz, 2 H, 14-H)

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.09 (q, C-13), 14.25 (q, C-15), 22.96 (t, C-12), 28.75 (2 x t, C-4 / 8), 29.56 (2 x t, C-5 / 7), 30.96 (t, C-11), 35.16 (t, C-10), 40.18 (d, C-2), 41.67 (2 x t, C-1 / 3), 41.87 (2 x d, C-3a / 8a), 43.41 (d, C-6), 59.96 (t, C-14), 176.08 (s, C-9).

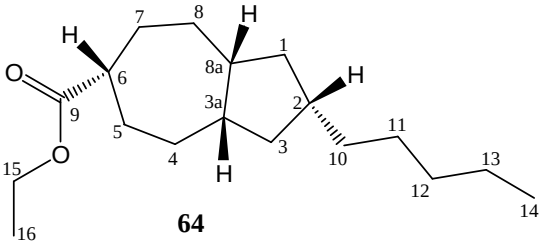
UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (3.95), 232 (2.60), 260 (2.37), 278 (2.30), 310 (2.18).

IR (film): $\tilde{\nu}$ = 2928 cm^{-1} (s, CH-stretching), 1462, 1378 (w), 1732 (s, C=O), 1182, 1160 (s, C-O).

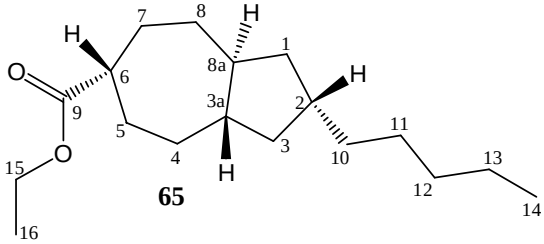
MS (EI, 70 eV): *m/z* (%) = 266 [M^+] (88), 237 [M^+-C_2H_5] (45), 220 [237-OH] (36), 251 [M^+-CH_3] (19), 209 [M^+-C_4H_9] (78), 163 [220-C_4H_9] (100), 135 [163-CO] (55).

HRMS ($C_{17}H_{30}O_2$): Calcd.266.2246; found 266.22431 ± 5 ppm.

4.2.9c. Ethyl 2-pentyl-perhydro-6-azulenecarboxylate (64/65)



64



65

The procedure for the hydrogenation of **59c** to get **64/65** was the same as described earlier for **59a** (0. 8 g (2.91 mmol) of **59c**; 0.2 g of Pd/C in 50 mL of EtOAc). In addition to **64/65** partially reduced compound **66** was also isolated (164 mg, 20 %) and characterized which on further hydrogenation quantitatively converted to **64/65**. Product **62/63** obtained as a colourless liquid. The spectroscopic and analytical data for **64** is given below.

Yield = 0.6 g, 73 %

R_F (SiO_2; (pentan/dichloromethane; 7:3) = 0.4

B. p. = 152 °C / 2 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 6.9 Hz, 3 H, 14-H), 1.27 (t, ^3J = 7.0 Hz, 3 H, 16-H), 1.24-1.33 (m, 8 H, side chain protons), 1.44-1.53 (m, 2 H, 3a / 8a-H), 1.54-1.66 (m, 4 H, 4 / 8-H), 1.68-1.69 (m, 1 H, 2-H), 0.76 / 1.72 (m, 4 H, 1 / 3-H), 1.91-2.10 (m, 4 H, 5 / 7-H), 2.13-2.18 (m, 1 H, 6-H), 4.13 (q, ^3J = 7.1 Hz, 2 H, 15-H).

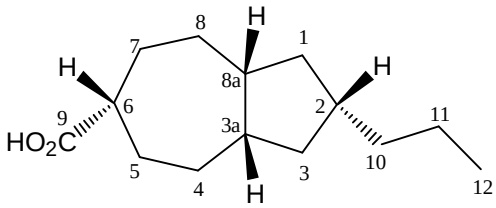
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.04 (q, C-14), 14.24 (q, C-16), 22.63 (t, C-13), 22.65 (t, C-12), 25.99 (2 x t, C-4 / 8), 28.75 (2 x t, C-5 / 7), 31.11 (t, C-11), 32.98 (t, C-10), 41.87 (d, C-2), 42.45 (2 x t, C-1 / 3), 42.96 (2 x d, C-3a / 8a), 43.40 (d, C-6), 59.99 (t, C-15), 176.49 (s, C-9).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 194 nm (3.78), 208 (3.45), 216 (3.32), 268 (2.06).

IR (film): $\tilde{\nu}$ = 2977 cm^{-1} (s, C-H stretching aliphatic), 1732 (s, C=O), 1462, 1449, 1378, 1298, 1288, 1236, 1221, 1201 (m), 1161 (s), 1035 (m).

MS (EI, 70 eV): *m/z* (%) = 280.3 [M^+] (100), 251.2 [M^+-C_2H_5] (65), 235.2 [M^+-C_2H_5O] (23), 209.2 [M^+-C_5H_{11}] (82), 180 [209.2-C_2H_5] (13), 165.2 [209.2-CO_2] (81), 151.1 [165.2-CH_2] (11), 135.1 [165.2-C_2H_6] (40).

4.2.10. 2-Propyl perhydro-6-azulenecarboxylic acid (73)



73

The procedure for the hydrolysis of the ethyl ester **60** of the above acid **73** was the same as described for **67** (1.0 g of **60**; 200 mL of EtOH and 120 mL of 1M NaOH). The product **73** was recrystallized from hexane/dichloromethane mixture to yield colourless monoclinic crystals.

Yield = 0.7 g, 79%

R_F (SiO_2; (dichloromethane) = 0.2

M. p. = 94-96 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.91 (t, ^{3}J = 6.96 Hz, 3 H, 12-H), 1.26-1.33 (m, 4 H, side chain protons), 1.48-1.53 (m, 2 H, 3a / 8a-H), 1.56-1.63 (m, 4 H, 4 / 8-H), 1.70-1.73 (m, 1 H, 2-H), 0.83 / 1.72 (m, 4 H, 1 / 3-H), 2.11-2.19 (m, 4 H, 5 / 7-H), 2.74 (m, 1 H, 6-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.39 (q, C-12), 21.78 (t, C-11), 28.78 (2 x t, C-4 / 8), 37.78 (t, C-10), 29.44 (2 x t, C-5 / 7), 41.71 (2 x t, C-1 / 3), 39.98 (d, C-2), 43.22 (d, C-6), 42.01 (2 x s, C-3a / 8a), 182.25 (s, C=O).

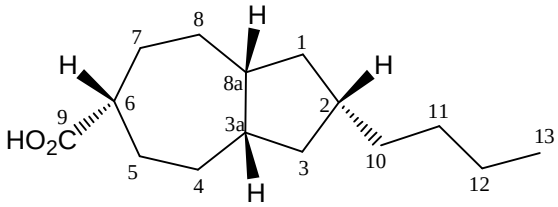
UV/Vis (MeOH): λ_{max} (lg ε) = 206 nm (3.58), 244 (3.19), 288 (2.52), 236 (3.12), 274 (2.42), 308 (2.03).

IR (KBr): $\tilde{\nu}$ = 3027 cm^{-1}, 2952, 2931, 2915, 2904, 2888, 2866, 2843 (s, C-H stretching aliphatic), 3380 (m), 2730, 2682, 2651, 2631, 2600, 2587, 2552 (w), 1700 (s, C=O), 1656, 1648 (w), 1451, 1426, 1403 (m), 1324, 1309, 1301 (w), 1283, 1266, 1241, 1213, 1192, 1151 (m).

MS (EI, 70 eV): *m/z* (%) = 224 [M^+] (40), 206 [M^+-H_2O] (15), 195 [M^+-C_2H_5] (30), 181 [M^+-C_3H_7] (100), 163 [181-H_2O] (25), 137 [181-CO_2] (80), 109 [137-C_2H_4] (45).

Elemental analysis $C_{14}H_{24}O_2$ (224): Calcd. C 74.94 %, H 10.79 %; found C 74.92 %, H 10.89 %.

4.2.11. 2-Butyl perhydro-6-azulenecarboxylic acid (74)



74

The procedure for the hydrolysis of the ethyl ester **62** of the above acid **74** was the same as described for **67** (50 mg of **62**; 10 mL of EtOH and 6 mL of 1M NaOH). The product **74** was recrystallized from hexane/dichloromethane mixture to yield colourless monoclinic crystals.

Yield = 40 mg, 89%

R_F (SiO_2; (dichloromethane) = 0.2

M. p. = 78-80 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.80 (t, ^3J = 6.73 Hz, 3 H, 13-H), 1.17-1.21 (m, 6 H, side chain protons), 1.23-1.42 (m, 2 H, 3a / 8a-H), 1.45-1.50 (m, 4 H, 4 / 8-H), 1.55-1.60 (m, 1 H, 2-H), 0.72 / 1.81 (m, 4 H, 1 / 3-H), 2.00-2.28 (m, 4 H, 5 / 7-H), 2.65 (m, 1 H, 6-H).

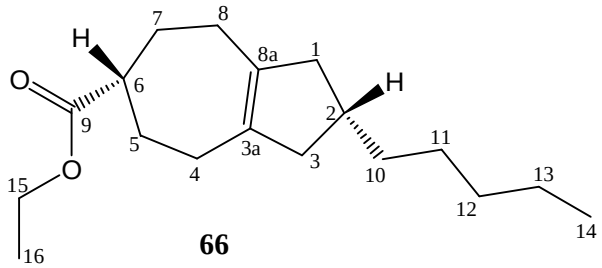
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.12 (q, C-13), 22.98 (t, C-12), 28.78 (2 x t, C-4 / 8), 30.96 (t, C-10), 29.49 (2 x t, C-5 / 7), 35.17 (t, C-11), 41.75 (2 x t, C-1 / 3), 40.23 (d, C-2), 43.06 (d, C-6), 42.01 (2 x s, C-3a / 8a), 180.93 (s, C-9).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 254 nm (3.22), 266 (3.19), 192 (4.24), 208 (3.92), 216 (3.74), 224 (3.54), 232 (3.32), 280 (3.13), 312 (2.75).

IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1}, 2931, 2921, 2892, 2870, 2855 (s, C-H stretching aliphatic), 3432 (m), 1697 (s, C=O), 1456 (m), 1274, 1248 (m).

MS (EI, 70 eV): *m/z* (%) = 238 [M^+] (49), 220 [M^+-H_2O] (19), 209 [M^+-C_2H_5] (44), 181 [M^+-C_4H_9] (100), 163 [181-H_2O] (34), 135 [181-HCO_2H] (49), 109 [135-C_2H_2] (50).

4.2.12. 2-Pentyl-1, 2, 3, 4, 5, 6, 7, 8-octahydro-azulene-6-carboxylic acid ethyl ester (66)



66

The above compound was obtained during the hydrogenation of **59c** to **64/65** in the presence of Pd-C/H_2 in EtOAc, which by increasing the time of hydrogenation was further converted to fully hydrogenated product **64/65**. Compound was obtained as a coloured liquid after purification by column chromatography on silica gel.

Yield = 164 mg, 20 %

R_F (SiO_2; (pentan/dichloromethane; 8:2) = 0.3

B. p. = 170 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.91 (t, ^3J = 6.88 Hz, 3 H, 14-H), 1.28 (t, ^3J = 7.0 Hz, 3 H, 16-H), 1.25-1.39 (m, 8 H, side chain protons), 169-1.76 (m, 4 H, 4 / 8-H), 1.77-1.81 (m, 1 H, 2-H), 1.01 / 1.99 (m, 4 H, 1 / 3-H), 2.00-2.13 (m, 4 H, 5 / 7-H), 2.15-2.25 (m, 1 H, 6-H), 4.14 (q, ^3J = 7.1 Hz, 2 H, 15-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.07 (q, C-14), 14.22 (q, C-16), 22.68 (t, C-13), 27.72 (2 x t, C-4 / 8), 26.15 (t, C-10), 32.05 (t, C-11), 29.56 (2 x t, C-5 / 7), 45.98 (2 x t, C-1 / 3), 33.01 (t, C-12), 36.67 (d, C-2), 46.27 (d, C-6), 60.09 (t, C-15), 135.85 (2 x s, C-3a / 8a), 176.48 (s, C-9).

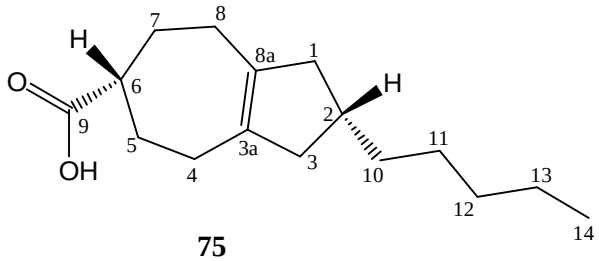
UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (3.75), 274 (2.50), 288 (2.50), 338 (2.30), 366 (2.28), 374 (2.25).

IR (film): $\tilde{\nu}$ = 2977 cm^{-1}, 2979, 2925, 2853 (s, C-H stretching aliphatic), 1736 (s, C=O), 1449, 1377, 1368, 1287, 1260, 1235 (m), 1117 (w), 1034 (w).

MS (EI, 70 eV): *m/z* (%) = 278 [M^+] (21), 234 [M^+-CO_2] (2), 232 [M^+-C_2H_5OH] (28), 204 [234-C_2H_4] (52), 161 [204-C_3H_7] (74), 147 [161-CH_2] (8), 133 [204-C_5H_{11}] (100), 119 [133-CH_2] (15), 105 [119-CH_2] (23).

HRMS ($C_{18}H_{30}O_2$): Calcd. 278.22458; found 278.22451 ± 3 ppm.

4.2.13. 2-Pentyl-1, 2, 3, 4, 5, 6, 7, 8-octahydro-azulene-6-carboxylic acid (75)



75

The procedure for the hydrolysis of the ethyl ester **66** of the above acid **75** was the same as described for **67** (100 mg (0.359 mmol) of **66**; 25 mL of EtOH and 15 mL of 1M NaOH). The product **75** obtained as a light coloured liquid.

Yield = 70 mg, 77 %

R_F (SiO_2; (dichloromethane) = 0.26

B. p. = 245 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.81 (t, ^3J = 6.88 Hz, 3 H, 14-H), 1.12-1.25 (m, 8 H, side chain protons), 1.56-1.71 (m, 4 H, 4 / 8-H), 1.72-1.74 (m, 1 H, 2-H), 0.90 / 1.92 (m, 4 H, 1 / 3-H), 1.96-2.16 (m, 4 H, 5 / 7-H), 2.31-2.37 (m, 1 H, 6-H).

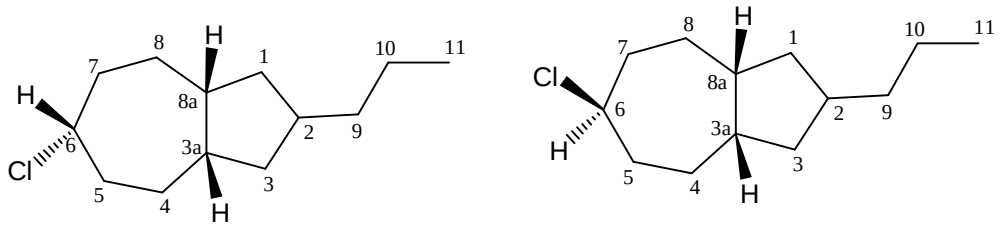
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.08 (q, C-14), 22.69 (t, C-13), 27.57 (2 x t, C-4 / 8), 25.98 (t, C-12), 29.28 (2 x t, C-5 / 7), 32.96 (t, C-11), 45.95 (2 x t, C-1 / 3), 36.69 (t, C-10), 36.73 (d, C-2), 46.13 (d, C-6), 135.83 (2 x s, C-3a / 8a), 182.46 (s, C-9).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (2.65).

IR (film): $\tilde{\nu}$ = 2924 cm^{-1}, 2871, 2854 (s, C-H stretching aliphatic), 1704 (s, C=O), 1450, 1417, 1298, 1265, 1235 (m), 1192 (w).

MS (EI, 70 eV): *m/z* (%) = 250.1 [M^+] (32), 204.2 [M^+-HCO_2H] (11), 179.1 [M^+-C_5H_{11}] (100), 161.1 [179.1-H_2O] (36), 133.1 [179.1-HCO_2H] (67), 107.1 [133.1-C_2H_2] (11).

4.2.14. 6-Chloro-2-propyl-decahydro-azulene (87)



87

N-Chlorosuccinimide (6.64g) and acid **73** (2.0 g, 8.92 mmol) were dissolved in dimethylformamide (20 mL) and glacial acetic acid (4 mL). The solution was freed of oxygen by repeated evacuation and admission of nitrogen. Lead tetraacetate (3.58 g, stabilized with ca. 15 % acetic acid) was added and the reaction mixture was again degassed. Warming at 40-50 °C initiated the exothermic evolution of carbon dioxide which was complete after 20 min. The solution was cooled and extracted with several portions of pentane. The pentane extractions were washed with 20 % of perchloric acid, 10 % of aqueous potassium carbonate and water, dried with sodium sulfate and finally the desired product was purified by column chromatography on silica gel eluting with pentane to furnish 1.3 g of chloride (mixture of two isomers) as clear oil.

Yield = 1.3 g, 68 %

$\mathbf{R_F}$ (SiO_2; (pentane) = 0.9

B. p. = 185 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.91 / 0.92 (2 x t, ^3J = 7.02 / 7.05 Hz, 3 H, 11-H), 1.11-1.20 (m, 4 H, side chain protons), 1.62-2.36 (m, 15 H, rest of the protons of both rings), 3.86 (tt, ^3J = 11.7 Hz, 4.1 Hz, 1 H, 6-H_β(axial), 4.53 (m, 1 H, 6-Hα (equatorial).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.40 (q, C-11), 21.79 (t, C-10), 26.12 (2 x t, C-4 / 8), 29.66 (2 x t, C-5 / 7), 37.65 (t, C-10), 40.28 (d, C-2), 40.40 (2 x t, C-1 / 3), 42.19 (2 x d, C-3a / 8a), 63.83 (d, C-6).

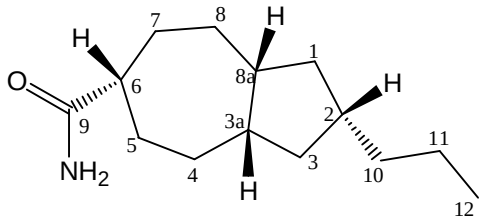
UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (2.37), 216 (1.72), 260 (1.04), 298 (8.34).

IR (film): $\tilde{\nu}$ = 2931 cm^{-1}, 2859 (s, C-H stretching), 1461 (m), 1442, 1428, 1378, 1240 (w).

MS (EI, 70 eV): *m/z* (%) = 214 [M^+] (7), 179 [M^+-Cl] (16), 178 [M^+-HCl] (100), 163 [178-CH_3] (21), 149 [178-C_2H_5] (42).

HRMS ($C_{13}H_{23}Cl$): Calcd. 214.1488; found 214.14831 $\pm$ 2 ppm.

4.2.15. 2-Propyl-decahydro-azulene-6-carboxylic acid amide (96)



96

To a suspension of acid **73** (0.5 g, 2.23 mmol) in 5 mL of chloroform was added $SOCl_2$ (5 mL) under nitrogen atmosphere, and the mixture refluxed for 3 h. When the TLC analysis showed no remaining acid, the reaction was stopped and the solvent as well as excess thionyl chloride were evaporated by rotary evaporation. Due to the instability of the chloride it was directly saturated with dry ammonia for 30 min and the reaction mixture concentrated to dryness. The residue was washed with water and air dried. After several washings with pentane and pentane/dichloromethane to remove impurities, the amide **96** (0.2 g) was obtained as a colourless solid.

Yield = 0.2 g, 40 %

R_F (SiO_2; (dichloromethane) = 0.1

M. p. = 188-190 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.80 (t, ^3J = 6.88 Hz, 3 H, 12-H), 1.08-1.27 (m, 4 H, side chain protons), 1.32-1.47 (m, 2 H, 3a / 8a-H), 1.52-1.58 (m, 4 H, 4 / 8-H), 1.59-1.68 (m, 1 H, 2-H), 0.67 / 1.71 (m, 4 H, 1 / 3-H), 1.84-1.97 (m, 4 H, 5 / 7-H), 2.05-2.09 (m, 1 H, 6-H), 5.23-5.26 (br. d, 2 H, NH_2).

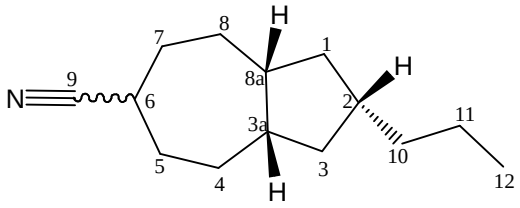
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.39 (q, C-12), 21.76 (t, C-11), 31.21 (2 x t, C-4 / 8), 32.96 (2 x t, C-5 / 7), 37.74 (t, C-10), 40.03 (d, C-2), 42.44 (2 x t, C-1 / 3), 42.96 (2 x d, C-3a / 8a), 43.99 (d, C-6), 179.05 (s, C-9).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (3.67), 212 (2.64), 220 (2.58), 226 (2.51), 242 (2.09), 274 (1.90).

IR (KBr): $\tilde{\nu}$ = 3382 cm^{-1} (s, C-H stretching), 3192 (m), 2952 (m), 2923, 2892, 2868, 2857, 2841 (m), 1651 (s, C=O), 1630 (m), 1455 (w), 1420 (w).

MS (EI, 70 eV): *m/z* (%) = 223 [M^+] (8), 206 [M^+-NH_3] (5), 180 [M^+-C_3H_7] (2), 163 [180-NH_3] (6), 135 [163v-CO] (3), 121 [135-CH_2] (5), 109 [135-C_2H_2] (3), 81 [109-C_2H_4] (8), 59 [CH_2CONH_3] (100).

4.2.16. 2-Propyl-decahydro-azulene-6-carbonitrile (97)



97

In a well-ventilated hood, trichloromethyl chloroformate (0.1 mL) was added dropwise to a cold (0-5 °C), stirred solution of the amide **96** (50 mg, 0.224 mmol) in trimethyl phosphate (1 mL). The reaction mixture was slowly heated to 60 °C for 10 min to ensure the completion of the reaction and also drive away any generated phosgene. After cooling with an ice-water bath, the reaction mixture was vigorously stirred and ice-water (5 g) was added to destroy any trace of phosgene and chloroformate. The mixture was extracted with three portions of dichloromethane and dried with $MgSO_4$. The solvent was evaporated in vacuo and the compound was purified by column chromatography on silica gel eluting with pentane and then pentane/dichloromethane mixture to yield 20 mg of a light coloured liquid which solidified below 0 °C.

Yield = 20 mg, 43 %

R_F (SiO_2; (dichloromethan/pentane; 1:1) = 0.7

M. p. = >5 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.80 (t, ^3J = 6.94 Hz, 3 H, 12-H), 1.10-1.25 (m, 4 H, side chain protons), 1.34-1.40 (m, 2 H, 3a / 8a-H), 1.45-1.62 (m, 4 H, 4 / 8-H), 1.64-1.66 (m, 1 H, 2-H), 0.77 / 1.86 (m, 4 H, 1 / 3-H), 1.89-2.12 (m, 4 H, 5 / 7-H), 2.35-2.40 (m, 1 H, 6-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.35 (q, C-12), 21.71 (t, C-11), 30.89 (2 x t, C-4 / 8), 31.53 (d, C-6), 33.11 (2 x t, C-5 / 7), 37.63 (t, C-10), 40.02 (d, C-2), 42.11 (2 x t, C-1 / 3), 42.61 (2 x d, C-3a / 8a), 123.10 (s, C-9).

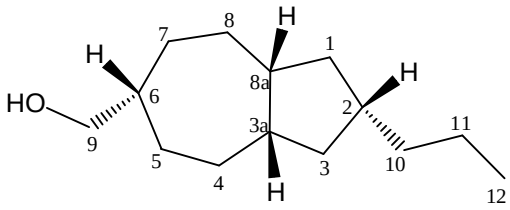
UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (3.81), 218 (2.65), 232 (2.17).

IR (film): $\tilde{\nu}$ = 2929 cm^{-1} (s, C-H stretching), 2859 (s), 2252, 2237 (w, CN), 1461 (m), 1377 (w).

MS (EI, 70 eV): *m/z* (%) = 205 [M^+] (8), 190 [M^+-CH_3] (12), 178 [M^+-HCN] (12), 177 [178-H] (100), 162 [177-CH_3] (55), 134 [177-C_3H_7] (38), 120 [134-CH_2] (29), 108 [134-C_2H_2] (58).

Elemental analysis $C_{14}H_{23}N$ (205.34): Calcd. C 81.89 %, H 11.29 %, N 6.82 %; found C 81.96 %, H 11.39 %, N 6.69 %.

4.2.17. (2-Propyl-decahydro-azulen-6-yl)-methanol (101)



101

To a mixture of $LiAlH_4$ (60.22 mg, 1.58 mmol) in THF (100 mL) was added dropwise 2-propyl-azulen-6-carboxylic-acid ethyl ester **60** (0.8 g, 3.17 mmol) dissolved in THF with a dropping funnel. Stirring was continued for further 30 min and then the mixture was refluxed for 12 h. The reaction mixture was cooled and ice-water was added dropwise to quench the reaction followed by a 10 % solution of HCl. The organic layer was extracted with diethyl ether (3 x 20 mL), dried with $MgSO_4$ and the solvent evaporated to provide the product mixture. After purification by column chromatography on silica gel with CH_2Cl_2 as an eluent 0.5 g (67 %) of the above alcohol **101** was obtained as a colourless liquid.

R_F (SiO_2; dichloromethan) = 0.5

B. p. = not measured due to small amount of material.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.83 (t, ^3J = 6.57 Hz, 2 H, 12-H), 1.14-1.37 (m, 4 H, side chain protons), 1.39-1.46 (m, 2 H, 3a / 8a-H), 1.45-1.60 (m, 4 H, 4 / 8-H), 1.62-1.70 (m, 1 H, 2-H), 0.71 / 1.76 (m, 4 H, 1 / 3-H), 1.83-2.0 (m, 4 H, 5 / 7-H), 2.03-2.12 (m, 1 H, 6-H), 2.51 (s, 1 H, OH), 3.30-3.34 (d, ^3J = 6.2 Hz, 2 H, 9-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.36 (q, C-12), 21.76 (t, C-11), 31.36 (2 x t, C-4 / 8), 32.50 (2 x t, C-5 / 7), 37.80 (t, C-10), 41.71 (d, C-2), 42.54 (2 x t, C-1 / 3), 43.11 (2 x d, C-3a / 8a), 45.51 (d, C-6), 68.79 (t, C-9).

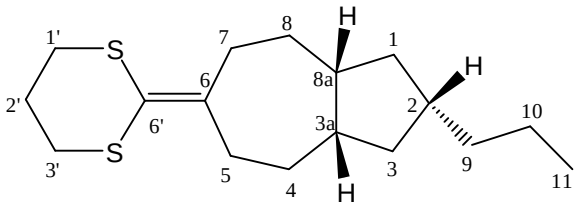
UV/Vis (CH_3CN): λ_{max} (lg ε) = 198 nm (3.35), 224 (2.68), 196 (3.34), 200 (3.34), 210 (2.82), 234 (2.56), 242 (2.32), 248 (2.04), 268 (1.76), 276 (1.83).

IR (film): $\tilde{\nu}$ = 3347 cm^{-1} (m, OH), 2955, 2921 (s, C-H stretching), 2869, 2858 (m), 1727 (w), 1460, 1378, 1288, 1274 (w).

MS (EI, 70 eV): *m/z* (%) = 192 [M^+-H_2O] (13), 163 [192-C_2H_5] (41), 149 [192-C_3H_7] (100), 135 [149-CH_2] (9), 109 [149-C_3H_4] (17), 95 [109-CH_2] (26), 81 [95-CH_2] (26).

Elemental analysis $C_{14}H_{26}O$ (210.36): Calcd. C 79.92 %, H 12.47 %; found C 79.23 %, H 12.55 %.

4.2.18. 6'-(2-Propyl-octahydro-azulen-6-ylidene)-[1', 3'] dithiane (107)



107

1,3-Propanedithiol (62.92 mg, 0.058 mL, 0.5813 mmol) was added to a suspension of 2-propyl-perhydroazulene-6-carboxylic acid **73** (100 mg, 0.446 mmol) in a mixture of toluene (3 mL) and isooctane (3 mL). The milky suspension was heated to 50 °C and trifluoromethanesulfonic acid (87.23 mg, 0.051 mL, 0.581 mmol) was added slowly. The resulting solution was heated to 102-104 °C and water formed during the reaction was removed azeotropically. The solution was cooled to 90 °C and methyl *tert*-butyl ether (0.5 mL) was added slowly at 90-70 °C. The dithianylium triflate of the reactant acid was not isolated and the reaction mixture was used directly for the next step.

A solution of 4-cyano-4'-hydroxy-biphenyl (58.5 mg, 0.3 mmol) in a mixture of triethylamine (0.035 mL) and dichloromethane (1 mL) was cooled to -70 °C. Then a solution of the above dithianylium salt **105** in dichloromethane was added slowly at the same temperature. After the mixture had been stirred for 1 h, NEt_3.3HF (0.2 mL, 1.25 mmol) was added, followed by a solution of bromine (0.064 mL, 1.25 mmol) in dichloromethane. The mixture was stirred for 1 h at the same temperature and after warming to 0 °C, the solution was poured into a mixture of 32 % aqueous NaOH (5 mL) and ice (10 g). The pH was adjusted to 5-8 by addition of 32 % aqueous NaOH solution. The aqueous layer was extracted with dichloromethane and filtered through celite, washed with water and

evaporated to dryness. The crude product was purified through a column of silica gel eluting with pentane and then pentane/dichloromethane mixture (8:2). The starting material **107** was obtained as a side product in 20 % yield (27 mg) while the desired product **106** could not be isolated.

R_F (SiO_2; dichloromethan/pentane; 2:8) = 0.5

M. p. = 54-56 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.79 (t, ^3J = 6.58 Hz, 3 H, 11-H), 1.15-1.20 (m, 4 H, side chain protons), 1.21-1.26 (m, 4 H, 4-H, 8-H), 1.59-1.63 (m, 2 H, 3a-H, 8a-H), 0.70 / 1.58 (m, 4 H, 1-H, 3-H), 1.81-1.84 (m, 1 H, 2-H), 1.99-2.06 (m, 4 H, 5-H, 7-H), 2.07-2.09 (m, 2 H, 2'-H), 2.70-2.84 (m, 4 H, 1'-H, 3'-H).

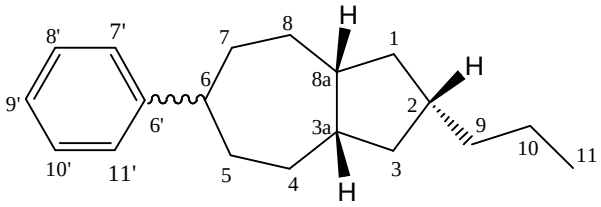
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.37 (q, C-11), 21.79 (t, C-10), 25.08 (t, C-2'), 30.36 (2 x t, C-1', C-3'), 33.29 (2 x t, C-4, C-8), 39.12 (t, C-9), 30.70 (2 x t, C-5, C-7), 41.23 (2 x t, C-1, C-3), 38.34 (d, C-2), 147.40 (2 x s, C-6, C-6'), 42.05 (2 x d, C-3a, C-8a).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (3.98), 212 (3.77), 218 (3.73), 228 (3.69), 238 (3.62), 282 (3.14), 296 (2.57).

IR (KBr): $\tilde{\nu}$ = 2934 cm^{-1}, 2921, 2910 (s, C-H stretching), 1462, 1453, 1435, 1419 (w), 1272, 1236 (w).

MS (EI, 70 eV): *m/z* (%) = 296 [M^+] (100), 189 [M^+-$C_3H_7S_2$] (26), 181 (35), 137 (29), 135 (16).

4.2.19. 6-Phenyl-2-propyl-decahydro-azulene (90)



90

10 mL of benzene and 1.7 g of anhydrous $AlCl_3$ were mixed thoroughly in a flask placed on a water bath. Chloride **87** of perhydroazulene (0.8 g, 3.73 mmol) obtained as described above was added dropwise. Gaseous HCl was evolved and the temperature was increased to about 35 °C. The mixture was heated for 4 h at 45-50 °C, cooled and poured onto ice; the organic layer was separated and washed with 5 % HCl solution and subsequently several times with

water. Excess benzene was removed under vacuum and the product was purified by column chromatography on silica gel eluting with pentane to get 0.6 g of a colourless liquid.

Yield = 0.6 g, 62 %

R_F (SiO_2; pentane) = 0.8

B. p. = 170-172 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.19 Hz, 3 H, 11-H), 0.99-1.09 (m, 4 H, side chain protons), 1.09-1.16 (m, 2 H, 3a / 8a-H), 1.17-1.39 (m, 4 H, 4 / 8-H), 1.60-1.63 (m, 1 H, 2-H), 0.87 / 1.72 (m, 4 H, 1 / 3-H), 1.73-1.90 (m, 4 H, 5 / 7-H), 2.15-2.20 (m, 1 H, 6-H), 7.11-7.52 (m, 5 H, aromatic protons).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.41 (q, C-11), 19.98 (t, C-10), 26.69 (2 x t, C-4 / 8), 33.38 (t, C-9), 33.94 (2 x t, C-5 / 7), 34.20 (d, C-2), 37.49 (d, C-6), 39.88 (2 x t, C-1 / 3), 43.07 (2 x d, C-3a / 8a), 112.5 (s, C-6'), 125.74 (d, C-9'), 126.80 (2 x d, C-7' / 11'), 128.24 (2 x d, C-8' / 10').

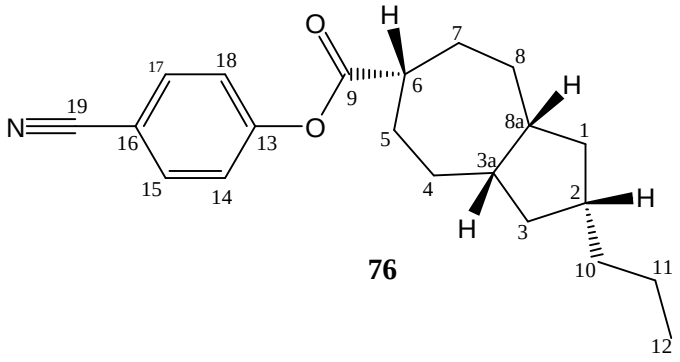
UV/Vis (CH_3CN): λ_{max} (lg ε) = 194 nm (4.42), 236 (3.70), 208 (3.94), 216 (3.90), 224 (3.70), 248 (3.28), 268 (3.03), 274 (3.06), 284 (3.03).

IR (film): $\tilde{\nu}$ = 3062 cm^{-1}, 3026 (w), 2953, 2917, 2850 (s, C-H stretching), 1493 (w), 1447 (m), 1376 (w).

MS (EI, 70 eV): *m/z* (%) = 256 [M^+] (20), 214 [M^+-C_3H_6] (15), 137 [214-C_6H_5] (47), 95 [137-C_3H_6] (91), 81 [95-CH_2] (100), 67 (81-CH_2] (47).

Although all the spectroscopic data were consistent with the proposed structure, the elemental analysis of this substance did not yield a satisfactory elemental composition.

4.2.20. 2-Propyl-decahydro-azulen-6-carboxylic acid 4-cyano-phenyl ester (76)



76

A solution of ethyl 2-propyl-perhydro-6-azulenecarboxylate **60** (50 mg, 0.1984 mmol) in benzene (dried, 20 mL) was treated with BBr_3 (49.70 mg, 0.1984 mmol) dissolved in benzene (20 mL) and the solution was stirred at 50 °C. After 5 h, 4-cyanophenol (23.63 mg, 0.1984 mmol) was added and the mixture was stirred at 50 °C for 15 h. After removal of the solvent, water was added and the mixture was neutralized with aqueous $NaHCO_3$ solution and extracted with EtOAc. The crude mixture was purified by preparative TLC with pentane: dichloromethane = 8:2 (v/v) to provide the product **76** (40 mg, 62 %) which was recrystallized from dichloromethane/hexane to yield clear colourless crystals. Excess phenol always reduced the reaction time as well as increased the yield of the new ester.

R_F (SiO_2, hexane/EtOAc, 9.5:0.5) = 0.5

M. p. = 87-90 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.80 (t, ^3J = 6.93 Hz, 3 H, 12-H), 1.16-1.23 (m, 4 H, side chain protons), 1.47-1.53 (m, 2 H, 3a / 8a-H), 1.54-1.59 (m, 4 H, 4 / 8-H), 1.61 (m, 1 H, 2-H), 0.73 / 1.83 (m, 4 H, 1 / 3-H), 2.12-2.19 (m, 4 H, 5 / 7-H), 2.86-2.89 (m, 1 H, 6-H), 7.12-7.14 (br. d, ^3J = 8.76 Hz, 2 H, 14 / 18-H), 7.59-7.62 (br. d, ^3J = 8.76 Hz, 2 H, 15 / 17-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.36 (q, C-12), 21.74 (t, C-11), 28.66 (2 x t, C-4 /8), 29.55 (2 x t, C-5 / 7), 37.73 (t, C-10), 39.95 (d, C-2), 41.66 (2 x t, C-1 / 3), 41.95 (2 x d, C-3a / 8a), 43.55 (d, C-6), 109.44 (s, C-16), 118.28 (s, C-19), 122.78 (2 x d, C-15 / 17), 133.55 (2 x d, C-14 / 18), 154.31 (s, C-13), 173.70 (s, C-9).

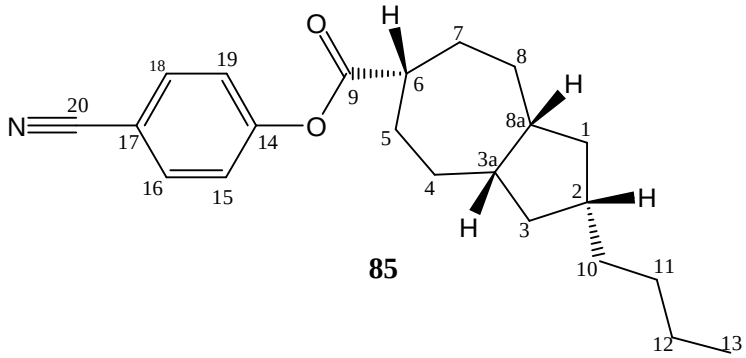
IR (KBr): $\tilde{\nu}$ = 3423 cm^{-1} (m), 3104, 3068 (m, CH-stretching, aromatic), 2952, 2927, 2917, 2893, 2858, 2838 (s, CH-stretching, aliphatic), 2228 (m, CN), 1749 (s, C=O), 1603, 1504, 1457(m), 1376 (w), 1211 (m), 1193 (m), 1167, 1156, 1127, 1105 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (4.64), 232 (4.24), 236 (4.22), 250 (3.53), 256 (3.14), 266 (3.01), 276 (2.86).

MS (EI, 70 eV): *m/z* (%) = 325 [M^+] (2.5), 207 [M^+-C_7H_4ON] (80), 179 [207-CO] (67), 123 [179-C_4H_8] (100), 109 [123-CH_2] (85), 95 [123-C_2H_4] (88), 81 [95-CH_2] (54).

Elemental analysis $C_{21}H_{27}O_2N$ (325.45): Calcd. C 77.50 %, H 8.36 %, N 4.30 %; found C 77.58 %, H 8.47 %, N 4.01 %.

4.2.21. 2-Butyl-decahydro-azulen-6-carboxylic acid 4-cyano-phenyl ester (85)



85

Yield = 42 mg, 65 %

R_F (SiO_2, pentane/dichloromethane, 8:2) = 0.5

M. p. = 88-90 °C (recrystallized from hexane/dichloromethane to yield colourless crystals).

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.86 (t, ^3J = 6.43 Hz, 3 H, 13-H), 1.24-1.44 (m, 6 H, side chain protons), 1.50-1.58 (m, 2 H, 3a / 8a-H), 1.60-1.65 (m, 4 H, 4 / 8-H), 1.67 (m, 1 H, 2-H), 0.80 / 2.10 (m, 4 H, 1 / 3-H), 2.18-2.28 (m, 4 H, 5 / 7-H), 2.94 (m, 1 H, 6-H), 7.17-7.25 (m, 2 H, 15 / 19-H), 7.64-7.70 (m, 2 H, 16 / 18-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.08 (q, C-13), 22.94 (t, C-12), 28.66 (2 x t, C-4 /8), 29.56 (2 x t, C-5 / 7), 30.92 (t, C-11), 35.12 (t, C-10), 40.20 (d, C-2), 41.71 (2 x t, C-1 / 3), 41.94 (2 x d, C-3a / 8a), 43.57 (d, C-6), 109 (s, C-17), 116 (s, C-20), 122.78 (2 x d, C-16 / 18), 133.58 (2 x d, C-15 / 19), 154.32 (s, C-14), 174 (s, C-9).

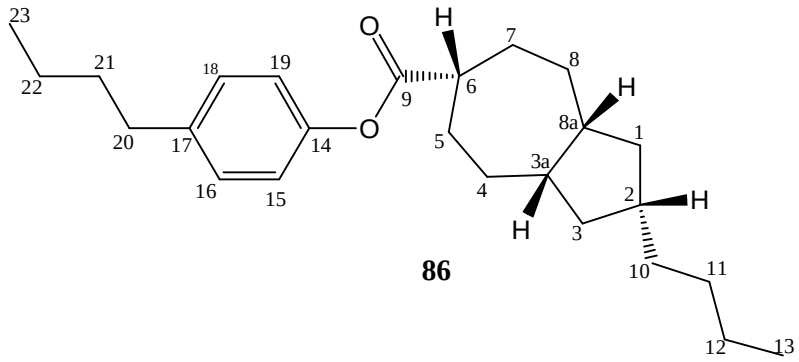
IR (KBr): $\tilde{\nu}$ = 3479 cm^{-1} (w), 3420 (w) 3070 (w, CH-stretching, aromatic), 2933, 2915 (s, CH-stretching, aliphatic), 2878, 2853, 2841 (m), 2230 (m, CN), 1750 (s, C=O), 1603, 1504, 1458 (m), 1451, 1440, 1376 (w), 1211 (m), 1168, 1156, 1125 (m), 1085, 1009 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (4.59), 234 (4.22), 198 (4.59), 222 (4.01), 244 (3.98), 250 (3.68), 260 (3.08).

MS (EI, 70 eV)**:** *m/z* (%) = 221 [M^+-C_7H_4ON] (100), 193 [221-CO] (81), 137 [193-C_4H_8] (45), 109 [137-C_2H_4] (48), 95 [109-CH_2] (60).

Elemental analysis $C_{22}H_{29}O_2N$ (339.48): Calcd. C 77.84 %, H 8.61 %, N 4.13 %; found C 77.36 %, H 8.46 %, N 4.17 %.

4.2.22. 2-Butyl-decahydro-azulen-6-carboxylic acid 4-butyl-phenyl ester (86)



86

Yield = 80 mg, 58 %

R_F (SiO_2, pentane/dichloromethane; 8:2) = 0.6

M. p. = 36-38 °C (light yellowish solid).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 6.83 Hz, 3 H, 13-H), 0.96 (t, ^3J = 7.31 Hz, 3 H, 23-H), 1.27-1.44 (m, 10 H, side chain protons), 1.58-1.60 (m, 2 H, 3a / 8a-H), 1.62-1.66 (m, 4 H, 4 / 8-H), 1.68-1.71 (m, 1 H, 2-H), 0.85 / 1.94 (m, 4 H, 1 / 3-H), 2.16-2.31 (m, 4 H, 5 / 7-H), 2.62-2.65 (t, ^3J = 7.71 Hz, 2 H, 20-H), 2.94-2.96 (m, 1 H, 6-H), 6.99-7.01 (br. d, ^3J = 8.44 Hz, 2 H, 15 / 19-H), 7.19-7.21 (br. d, ^3J = 8.45 Hz, 2 H, 16 / 18-H).

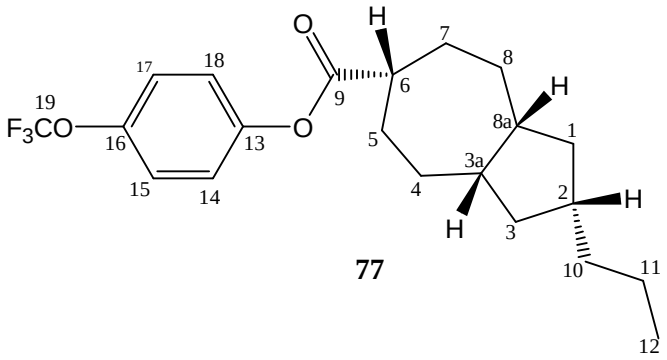
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.90 (q, C-13), 14.11 (q, C-23), 22.26 (t, C-22), 22.97 (t, C-12), 28.76 (2 x t, C-4 /8), 29.70 (2 x t, C-5 / 7), 30.97 (t, C-11), 33.61 (t, C-21), 35.01 (t, C-10), 35.18 (t, C-20), 40.24 (d, C-2), 41.76 (2 x t, C-1 / 3), 42.02 (2 x d, C-3a / 8a), 43.52 (d, C-6), 121.21 (2 x d, C-16 / 18), 129.17 (2 x d, C-15 / 29), 140.14 (s, C-17), 148.84 (s, C-14), 174.77 (s, C-9).

IR (KBr): $\tilde{\nu}$ = 3034 cm^{-1} (w), 2955, 2928 (s, CH-stretching, aliphatic), 2871, 2857 (m), 1755 (s, C=O), 1507 (m), 1460, 1378, 1299 (w), 1195, 1166, 1129 (m), 1018 (w).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 194 nm (4.55), 210 (3.95), 218 (3.93), 266 (2.96).

MS (EI, 70 eV)**:** *m/z* (%) = 370 [M^+] (5), 220 [M^+-$C_{10}H_{14}O$] (5), 152 [220-C_4H_4O] (100), 137 [152-CH_3] (55).

4.2.23. 2-Propyl-decahydro-azulen-6-carboxylic acid 4-(trifluoromethoxy)-phenyl ester (77)



77

Yield = 40 mg, 63 %

R_F (SiO_2, pentane) = 0.5

M. p. = 35-37 °C (colourless needles from hexane/dichloromethane).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.80 (t, ^3J = 6.94 Hz, 3 H, 12-H), 1.15-1.23 (m, 4 H, side chain protons), 1.48-1.51 (m, 2 H, 3a / 8a-H), 1.53-1.59 (m, 4 H, 4 / 8-H), 1.60-1.64 (m, 1 H, 2-H), 0.73 / 1.83 (m, 4 H, 1 / 3-H), 2.02-2.19 (m, 4 H, 5 / 7-H), 2.84-2.87 (m, 1 H, 6-H), 7.01-7.03 (br. d, ^3J = 9.05 Hz, 2 H, 15 / 17-H), 7.13-7.15 (br. d, ^3J = 9.03, 2 H, 14 / 18-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.37 (q, C-12), 21.78 (t, C-11), 28.71 (2 x t, C-4 / 8), 29.64 (2 x t, C-5 / 7), 37.78 (t, C-10), 40.0 (d, C-2), 41.71 (2 x t, C-1 / 3), 42.01 (2 x d, C-3a / 8a), 43.49 (d, C-6), 119.14 (s, C-19), 122.04 (2 x d, C-15 / 17), 122.91 (2 x d, C-14 / 18), 146.38 (s, C-13), 149.22 (s, C-16), 174.33 (s, C-9).

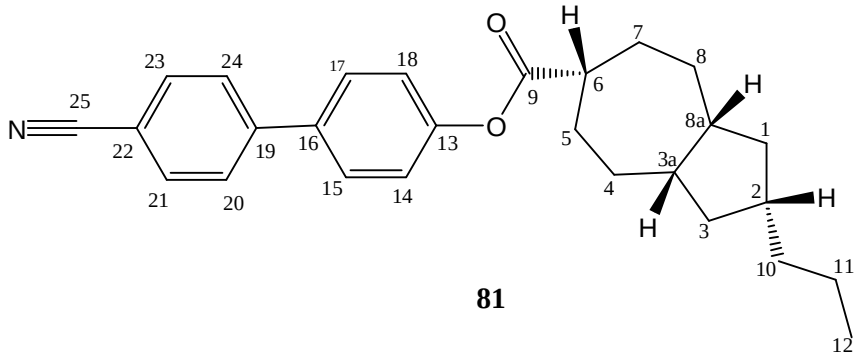
IR (KBr): $\tilde{\nu}$ = 3423 cm^{-1} (m), 2954, 2938, 2920 (s, CH-stretching), 2893, 2872, 2858, 2842 (s), 1751 (s, C=O), 1503 (s), 1459, 1450 (s), 1378, 1348, 1274, 1266, 1228, 1221, 1190, 1165, 1128 (s), 1099, 1086, 1048, 1013, 1005 (s).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 190 nm (4.45), 204 (3.93), 214 (3.79), 222 (3.53), 232 (3.04), 252 (2.74), 262 (2.84), 276 (2.58).

MS (EI, 70 eV): *m/z* (%) = 384 [M^+] (6), 207 [M^+-$C_7H_4O_2F_3$] (100), 179 [207-CO] (68), 178 [179-H] (15), 163 [178-CH_3] (9), 123 [163-C_3H_4] (41), 109 [123-CH_2] (44), 95 [109-CH_2] (48), 81 [109-C_2H_4] (30).

Elemental analysis $C_{21}H_{27}O_3F_3$ (384.44): Calcd. C 65.61 %, H 7.08 %; found C 65.44 %, H 7.16 %.

4.2.24. 2-Propyl-decahydro-azulene-6-carboxylic acid 4-cyano-4'-biphenyl ester (81)



81

The procedures for the synthesis of the *cis*-and *trans*-fused systems **81** and **83** respectively were the same as described above for **76**. However, preparative TLC was employed for the final purification of the product with pentane: CH_2Cl_2 (3:1) to yield the ***cis***- (**81**) as a clear colourless solid (44 mg, 55 %) while the ***trans***-isomer (**83**) was obtained as a yellowish solid (61 mg, 76 %).

R_F (SiO_2, Pentane/CH_2Cl_2; 7:3) = 0.4 (*cis*), 0.38 (*trans*)

M. p. = 101-105 °C (**81**); 99-102 °C (**83**)

The spectroscopic data for **81** are given below.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.80 (t, ^3J = 6.93 Hz, 3 H, 12-H), 1.17-1.24 (m, 4 H, side chain protons), 1.48-1.58 (m, 2 H, 3a / 8a-H), 1.60-1.64 (m, 4 H, 4 / 8-H), 1.65-1.67 (m, 1 H, 2-H), 0.75 / 1.84 (m, 4 H, 1 / 3-H), 2.17-2.22 (m, 4 H, 5 / 7-H), 2.87-2.90 (m, 1 H, 6-H), 7.11-7.13 (br. d, ^3J = 8.61 Hz, 2 H, 14 / 18-H), 7.50-7.53 (br. d, ^3J = 8.65 Hz, 2 H, 15 / 17-H), 7.57-7.59 (br. d, ^3J = 8.50 Hz, 2 H, 21 / 23-H), 7.64-7.66 (br. d, ^3J = 8.50 Hz, 2 H, 20 / 24-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.39 (q, C-12), 21.78 (t, C-11), 28.74 (2 x t, C-4 / 8), 29.67 (2 x t, C-5 / 7), 37.79 (t, C-10), 39.99 (d, C-2), 41.72 (2 x t, C-1 / 3), 42.00 (2 x d, C-3a / 8a), 43.59 (d, C-6), 110.97 (s, C-22), 118.85 (s, C-25), 122.38 (2 x d, C-14 / 18), 127.66 (2 x d, C-15 / 17), 128.25 (2 x d, C-20 / 24), 132.62 (2 x d, C-21 / 23), 136.61 (s, C-16), 144.86 (s, C-19), 151.47 (s, C-13), 174.51 (s, C-9).

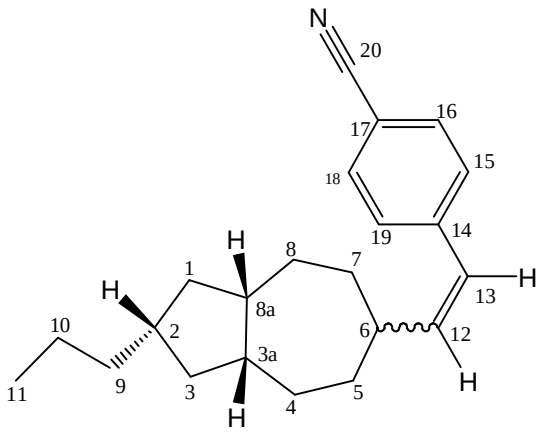
IR (KBr): $\tilde{\nu}$ = 3449 cm^{-1} (m), 3050, 3044 (m, CH-stretching), 2965, 2948, 2915 (s, CH-stretching), 2889, 2859, 2839 (s), 2224 (s, CN), 1745 (s, C=O), 1606, 1493, 1457, 1449 (s), 1365, 1216, 1195, 1182, 116, 1131 (s), 1091, 1083, 1046, 1002 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 200 nm (4.67), 272 (4.48), 208 (4.50), 212 (4.42), 214 (4.39), 222 (4.12), 292 (4.24), 302 (3.79).

MS (EI, 70 eV): *m/z* (%) = 401 [M^+] (19), 207 [M^+-$C_{13}H_8ON$] (55), 206 [207-H] (100), 179 [207-CO] (60), 166 [179-CH] (9), 137 [166-C_2H_5] (16), 109 [137-C_2H_4] (47), 95 [109-CH_2] (51).

Elemental analysis $C_{27}H_{31}NO_2$ (401.235): Calcd. C 80.76 %, H 7.78 %, N 3.49 %; found C 80.55 %, H 8.08 %, N 3.50 %.

4.2.25. 4-[2-[2-Propyl-decahydro-azulen-6-yl]-vinyl]-benzonitrile (104)



104

A mixture of **101** (0.2 g, 0.9523 mmol) and $Ph_3P.HBr$ (0.326 g, 0.9523 mmol) was heated at 160 ^oC for 2 h in a sealed tube to prepare the Wittig salt. The mixture was cooled to room temperature and concentrated in vacuo to leave a sticky oil which was triturated with anhydrous ether to give a solid which was further dried under vacuum to afford the Wittig salt. To the cooled Wittig salt in THF (20 mL, dry) at -30 °C KO^t-Bu (56.1 mg, 0.5 mmol) was added and the mixture stirred for 2 h. p-Cyanobenzaldehyde (0.367 g, 0.28 mmol) in dry THF (10 mL) was added dropwise and stirring continued overnight. To quench the reaction, water was added and the reaction mixture extracted with CH_2Cl_2, the combined washings were washed with water, dried with $MgSO_4$ and the solvent was evaporated in vacuo. The product mixture was purified by column chromatography on silica gel with pentane: CH_2Cl_2 (7:3) to yield 0.12g, 0.390 mmol, 40 % of **104** as a clear colourless solid.

R_F (SiO_2, pentane/CH_2Cl_2, 7:3) = 0.4

M. p. = 37-39 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.80 (t, ^{3}J = 6.17 Hz, 3 H, 11-H), 1.08-1.26 (m, 4 H, side chain protons), 1.42-1.45 (m, 2 H, 3a / 8a-H), 1.47-1.57 (m, 4 H, 4 / 8-H), 1.60-1.64 (m, 1 H, 2-H), 0.76 / 1.79 (m, 4 H, 1 / 3-H), 1.81-2.05 (m, 4 H, 5 / 7-H), 2.40-2.44 (m, 1 H, 6-H), 5.52 (dd, $^{3}J_{12\text{-H, }13\text{-H}}$ = 11.7 Hz, $^{3}J_{12\text{-H, }6\text{-H}}$ = 11.6 Hz, 1 H, 12-H), 6.14 (d, ^{3}J = 11.7 Hz, 1 H, 13-H), 7.22-7.28 (m, 2 H, 15 / 19-H), 7.52-7.55 (m, 2 H, 16 / 18-H).

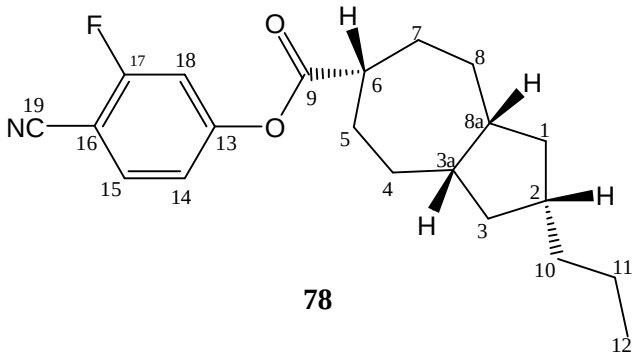
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.44 (q, C-11), 21.82 (t, C-10), 28.02 (2 x t, C-4 / 8), 31.42 (2 x t, C-5 / 7), 32.92 (t, C-9), 35.85 (d, C-2), 36.18 (2 x t, C-1 / 3), 41.56 (2 x d, C-3a / 8a), 42.57 (d, C-6), 109.88 (s, C-17), 119.12 (s, C-20), 124.37 (d, C-13), 129.21 (2 x d, C-15 / 19), 132.05 (2 x d, C-16 / 18), 142.48 (d, C-12), 142.72 (s, C-14).

IR (KBr): $\tilde{\nu}$ = 3005 cm^{-1} (w, CH-stretching), 2954, 2921, 2869, 2849 (m, CH-stretching), 2227 (m, CN), 1604, 1460, 1176 (w).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 268 nm (4.24), 192 (4.38), 198 (4.35), 210 (4.02), 214 (3.97), 218 (3.97), 286 (4.00), 294 (3.66), 300 (3.21).

MS (EI, 70 eV): *m/z* (%) = 307 [M^+] (5), 264 [M^+-C_3H_7] (7), 193 [M^+-C_8H_4N] (74), 149 [264-C_8H_5N] (100), 123 [149-C_2H_2] (67), 109 [123-CH_2] (80), 95 [109-CH_2] (85).

4.2.26. 2-Propyl-decahydro-azulen-6-carboxylic acid 4-cyano-3-fluoro-phenyl ester (78)



78

The procedure for the synthesis of **78** from **60** was the same as described before for **76** (50 mg (0.1984 mmol) of **60**; 49.70 mg (0.1984 mmol) of BBr_3; 27.2 mg of 2-fluoro-4-hydroxy benzonitrile in 20 mL of benzene). The product **78** was recrystallized from hexane to yield colourless needles.

Yield = 40 mg, 59 %

R_F (SiO_2, pentane/CH_2Cl_2; 7:3) = 0.5

M. p. = 59-62 °C

^{1}H NMR (400.1MHz, $CDCl_3$): δ = 0.91 (t, ^{3}J = 6.94 Hz, 3 H, 12-H), 1.27-1.34 (m, 4 H, side chain protons), 1.55-1.62 (m, 2 H, 3a / 8a-H), 1.65-1.71 (m, 4 H, 4 / 8-H), 1.72-1.74 (m, 1 H, 2-H), 0.84 / 1.95 (m, 4 H, 1 / 3-H), 2.16-2.29 (m, 4 H, 5 / 7-H), 2.98-3.01 (m, 1 H, 6-H), 7.06-7.08 (m, 2 H, 14 / 18-H), 7.66-7.69 (m, 1 H, 15-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.39 (q, C-12), 21.77 (t, C-11), 28.64 (2 x t, C-4 / 8), 29.53 (2 x t, C-5 / 7), 37.74 (t, C-10), 39.98 (d, C-2), 41.68 (2 x t, C-1 / 3), 41.98 (2 x d, C-3a / 8a), 43.61 (d, C-6), 98.64 (s, C-16), 110.76 (d, C-18), 113.51 (s, C-19), 118.60 (d, C-14), 133.92 (d, C-15), 155.68 (s, C-13), 162.29 (s, C-17), 173.26 (s, C-9).

^{19}F NMR (376.4 MHz, $CDCl_3$): δ = -104.08 (s, Ar-3-*F*).

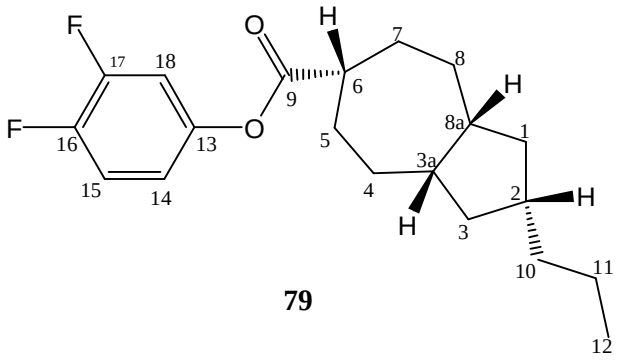
IR (KBr): $\tilde{\nu}$ = 3484 cm^{-1} (w), 3422 (w) 3111, 3070, 3053 (m, CH-stretching), 2959, 2923 (s, CH-stretching), 2890, 2878, 2861, 2841 (m), 2240 (m, CN), 1750 (s, C=O), 1616, 1582, 1499, 1460, 1452, 1433 (m), 1364, 1282, 1197, 1153, 1125 (s), 1104, 1183, 1004 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (4.57), 232 (4.22), 272 (3.31), 280 (3.31), 198 (4.56), 262 (3.08), 268 (3.22).

MS (EI, 70 eV): *m/z* (%) = 343 [M^+] (1), 207 [M^+-C_7H_3ONF] (100), 179 [207-CO] (98), 163 [207-C_3H_8] (26), 137 [163-C_2H_2] (30), 123 [137-CH_2] (61), 109 [137-CO] (67), 95 [109-CH_2] (70).

Elemental analysis $C_{21}H_{26}O_2NF$ (343.44): Calcd. C 73.44 %, H 7.63 %, N 4.08 %; found C 73.34 %, H 7.68 %, N 3.92 %.

4.2.27. 2-Propyl-decahydro-azulen-6-carboxylic acid 3, 4-difluoro-phenyl ester (79)



79

The procedure for the synthesis of **79** from **60** was the same as described before for **76** (50 mg (0.1984 mmol) of **60**; 49.70 mg (0.1984 mmol) of BBr_3; 25.8 mg of 3,4-difluorophenol in 20 mL of benzene). The product **79** was obtained as a light yellowish solid which could not be recrystallized.

Yield = 35 mg, 53 %

R_F (SiO_2, pentane/CH_2Cl_2; 8:2) = 0.5

M. p. = 34-36 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.80 (t, ^3J = 6.93 Hz, 3 H, 12-H), 1.16-1.22 (m, 4 H, side chain protons), 1.43-1.51 (m, 2 H, 3a / 8a-H), 1.52-1.58 (m, 4 H, 4 / 8-H), 1.59-1.65 (m, 1 H, 2-H), 0.73 / 1.83 (m, 4 H, 1 / 3-H), 2.02-2.17 (m, 4 H, 5 / 7-H), 2.82-2.85 (m, 1 H, 6-H), 6.72-6.75 (m, 1 H, 18-H), 6.85-6.90 (m, 1 H, 14-H), 7.06-7.18 (m, 1 H, 15-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.37 (q, C-12), 21.77 (t, C-11), 28.68 (2 x t, C-4 / 8), 29.59 (2 x t, C-5 / 7), 37.75 (t, C-10), 39.98 (d, C-2), 41.68 (2 x t, C-1 / 3), 41.98 (2 x d, C-3a / 8a), 43.44 (d, C-6), 111.73 (d, C-18), 117.04 (d, C-14), 117.58 (d, C-15), 146.58 / 148.88 (s, C-16), 146.81 / 149.26 (s, C-17), 151.37 (s, C-13), 174.19 (s, C-9).

^{19}F NMR (374.4 MHz, $CDCl_3$): δ = -141.89 / -141.83, -135.43 / -135.38 (2 X d, ^3J = 21.2 Hz, 2F, Ar-3,4-*F*).

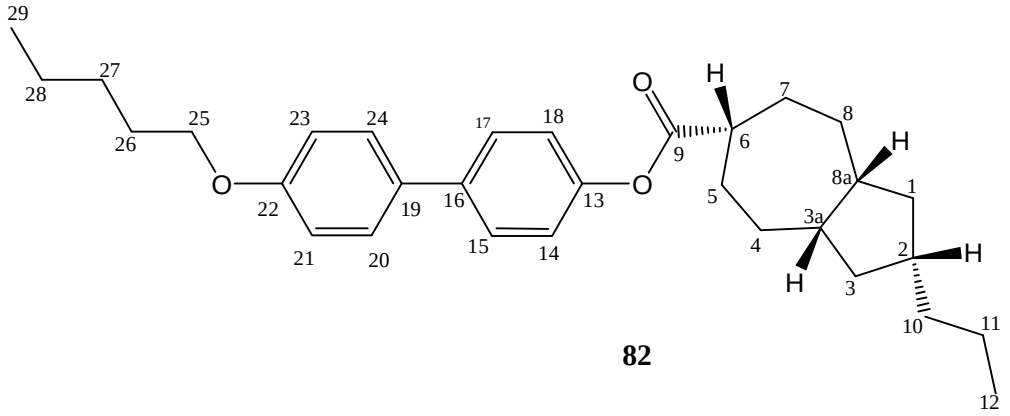
IR (KBr): $\tilde{\nu}$ = 3482 cm^{-1} (w), 3083, 3058 (m, CH-stretching), 2958, 2931 (s, CH-stretching), 2871, 2858, 2841 (m), 1750 (s, C=O), 1621, 1514 (s), 1459, 1436, 1297, 1253 (w), 1202, 1157, 1144, 1119, 1099 (m), 1083, 1003 (w).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 264 nm (3.10), 192 (4.28), 202 (3.92), 208 (3.83), 214 (3.61), 222 (3.33), 232 (2.83).

MS (EI, 70 eV)**:** *m/z* (%) = 336 [M^+] (25), 207 [M^+-$C_6H_3OF_2$] (100), 179 [207-CO] (85), 163 [207-C_3H_8] (8), 137 [163-C_2H_2] (15), 123 [137-CH_2] (52), 109 [137-CO] (50), 95 [109-CH_2] (52).

Elemental analysis $C_{20}H_{26}O_2F_2$ (336.42): Calcd. C 71.40 %, H 7.79 %; found C 71.67 %, H 7.79 %.

4.2.28. 2-Propyl-decahydro-azulen-6-carboxylic acid 4'-pentyloxy-biphenyl-4-yl ester (82)



82

The procedure for the synthesis of **82** from **60** was the same as described before for **76** (50 mg (0.1984 mmol) of **60**; 49.70 mg (0.1984 mmol) of BBr_3; 50.79 mg of 4-pentyloxy-phenol in 20 mL of benzene). The product **82** obtained as a light coloured powder which could not be recrystallized.

Yield = 48 mg, 52 %

R_F (SiO_2, pentane/CH_2Cl_2; 2:1) = 0.5

M. p. = 92-94 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.81 (t, ^3J = 6.73 Hz, 3 H, 12-H), 0.87 (t, ^3J = 7.1 Hz, 3 H, 29-H), 1.15-1.24 (m, 4 H, 11-H, 10-H), 1.31-1.39 (m, 4 H, 28-H, 27-H), 1.50-1.54 (m, 2 H, 3a / 8a-H), 1.55-1.61 (m, 4 H, 4 / 8-H), 1.62-1.67 (m, 1 H, 2-H), 1.71-1.75 (m, 2 H, 26-H), 0.75 / 1.83 (m, 4 H, 1 / 3-H), 2.16-2.22 (m, 4 H, 5 / 7-H), 2.86-3.38 (m, 1 H, 6-H), 3.90-3.93 (t, ^3J = 6.58 Hz, 2 H, 25-H), 6.87-6.89 (br. d, ^3J = 8.74 Hz, 2 H, 21 / 23-H), 7.02-7.04 (br. d, ^3J = 8.59 Hz, 2 H, 14 / 18-H), 7.39-7.41 (br. d, ^3J = 8.71 Hz, 2 H, 20 / 24-H), 7.44-7.46 (br. d, ^3J = 8.60 Hz, 2 H, 15 / 17-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.02 (q, C-12), 14.40 (q, C-29), 21.79 (t, C-11), 22.46 (t, C-28), 28.20 (2 x t, C-4 / 8), 28.76 (2 x t, C-5 / 7), 28.97 (t, C-27), 29.70 (t, C-26), 37.79 (t, C-10), 40.00 (d, C-2), 41.72 (2 x t, C-1 / 3), 42.02 (2 x d, C-3a / 8a), 43.56 (d, C-6), 68.07 (t, C-25), 114.77 (2 x d, C-21/23), 121.79 (2 x d, C-14/18), 127.59 (2 x d, C-15/17), 128.06 (2 x d, C-20/24), 132.79 (s, C-19), 138.43 (s, C-16), 149.86 (s, C-13), 158.71 (s, C-22), 174.70 (s, C-9).

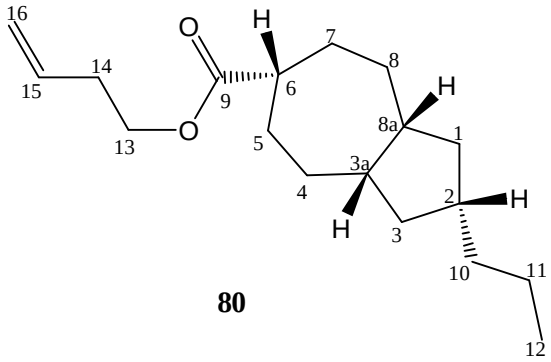
IR (KBr): $\tilde{\nu}$ = 3441 cm^{-1} (w), 3433 (w) 3041 (w, CH-stretching), 2957, 2931 (s, CH-stretching), 2872, 2859, 2842 (s), 1749 (s, C=O), 1607 (w), 1499 (s), 1460, 1438, 1392,

1378, 1369, 1322, 1308, 1288 (w), 1267, 1251 (m), 1217 (s), 1186 (w), 1169, 1131 (s), 1083, 1051, 1029 (w), 1014, 1000 (w).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 200 nm (4.65), 266 (4.36), 202 (4.64), 280 (4.22), 292 (3.86), 302 (3.28).

MS (EI, 70 eV): *m/z* (%) = 462 [M^+] (5), 256 [$C_{17}H_{20}O_2$] (100), 207 [$C_{14}H_{23}O$] (13), 186 [256-C_5H_{10}] (54), 179 [207-CO] (21), 137 [179-C_3H_6] (9), 123 [137-CH_2] (29), 95 [123-C_2H_4] (39).

4.2.29. 2-Propyl-decahydro-azulen-6-carboxylic acid but-3-enyl ester (80)



80

The procedure for the synthesis of **80** from **60** was the same as described before for **76** (50 mg (0.1984 mmol) of **60**; 49.70 mg (0.1984 mmol) of BBr_3; 14.3 mg (0.1984 mmol) of 1-butenol in 20 mL of benzene). The product **80** obtained as a colourless liquid.

Yield = 55 mg, 97 %

R_F (SiO_2; pentane/CH_2Cl_2; 7:3) = 0.4

B. p. = 133-135 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.80 (t, ^3J = 6.95 Hz, 3 H, 12-H), 1.14-1.22 (m, 4 H, side chain protons), 1.39-1.42 (m, 2 H, 3a / 8a-H), 1.45-1.47 (m, 4 H, 4 / 8-H), 1.48-1.61 (m, 1 H, 2-H), 0.69 / 1.79 (m, 4 H, 1 / 3-H), 1.98-2.05 (m, 4 H, 5 / 7-H), 2.29-2.34 (m, 2 H, 14-H), 2.55-2.58 (m, 1 H, 6-H), 4.06 (t, ^3J = 6.64, 2 H, 13-H), 5.00-5.06 (m, 2 H, 16-H), 5.6-5.7 (m, 1 H, 15-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.39 (q, C-12), 21.79 (t, C-11), 28.81 (2 x t, C-4 / 8), 29.62 (2 x t, C-5 / 7), 33.20 (t, C-14), 37.81 (t, C-10), 39.97 (d, C-2), 41.68 (2 x t, C-1 / 3), 41.95 (2 x d, C-3a / 8a), 43.44 (d, C-6), 63.10 (t, C-13), 117.06 (t, C-16), 134.22 (d, C-15), 176.04 (s, C=O).

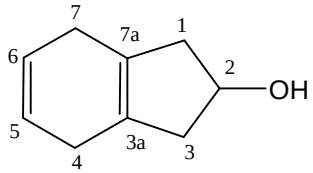
IR (film): $\tilde{\nu}$ = 2929 cm^{-1}, 2859 (s, CH-stretching), 1732 (s, C=O), 1642 (w), 1461, (m), 1180, 1142 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (3.00), 208 (2.05), 246 (1.38), 264 (1.30), 296 (1.23).

MS (GC / MS): *m/z* (%) = 278.2 [M^+] (7), 249 [M^+-C_2H_5] (8), 235 [M^+-C_3H_7] (9), 223 [M^+-C_4H_7] (11), 207 [M^+-C_4H_7O] (65), 179 [207-CO] (50), 205 [223-H_2O] (47), 177 [205-CO] (100), 164 [235-C_4H_7O] (10), 123 [179-C_4H_8] (40), 109 [123-CH_2] (47), 95 [109-CH_2] (47).

HRMS ($C_{18}H_{30}O_2$): Calcd. 278.2246; found 278.22549 ± 2 ppm.

4.2.30. 4-7-Dihydro-2-indanol (109)



109

2-Indanol (**36**, 5.0 g; 37.26 mmol), liquid NH_3 (30 mL), EtOH (30 mL) and THF (20 mL, anhydrous) were placed in a 500 mL three-necked flask fitted with a mechanical stirrer and the temperature maintained at –75 °C with a methanol-liquid nitrogen bath. Sodium metal was added until the blue colour persisted for 20 min. The NH_3 was allowed to evaporate overnight. The remaining residue was partitioned between ether and water. The ether layer was evaporated and the resulting liquid was again partitioned between ether and water. The ether layer was dried with $MgSO_4$ and the ether evaporated to give crude 4,7-dihydro-2-indanol (4.91 g, 97 %) as a colourless solid which melted above room temperature. The product was rather unstable and on standing slowly reoxidized to 2-indanol; it was thus readily used for further reaction.

R_F (SiO_2; ether/pentane; 1:2) = 0.3

M. p. = 36 °C (Lit.[85])

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.23-2.64 (m, 4 H, 1 / 3-H), 2.64-2.75 (m, 4 H, 4 / 7-H), 4.51-4.55 (m, 1 H, 2-H), 5.77 (s, 2 H, 5 / 6-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.57 (t, C-4 / 7), 46.02 (t, C-1 / 3), 70.83 (d, C-2), 124.75 (d, C-5 / 6), 129.77 (s, C-3a / 7a).

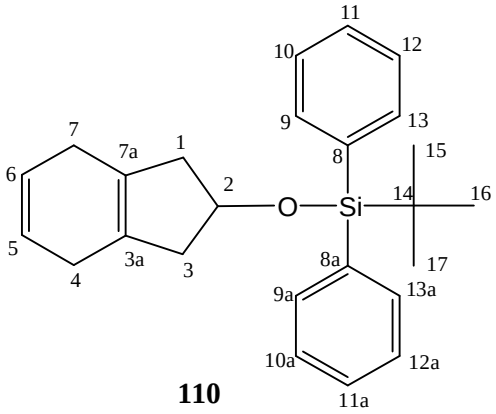
IR (film): $\tilde{\nu}$ = 3330 cm^{-1} (s, OH), 2912, 2818 (s, CH-stretching), 1430, 1291 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 194 nm (4.06), 204 (3.65), 212 (3.48), 218 (3.31), 224 (2.90), 266 (2.50), 274 (2.49).

MS (EI, 70 eV): *m/z* (%) = 136 [M^+] (35), 119 [M^+-OH] (5), 117 [119-H_2] (77), 92 [M^+-C_2H_4O] (70), 91[92-H] (100), 79 [92-CH] (30), 77 [91-CH_2] (23).

Elemental analysis $C_9H_{12}O$ (136.19): Calcd. C 79.37 %, H 8.88 %, O 11.75 %; found C 79.57 %, H 9.02 %.

4.2.31. 2-(tert-Butyl-diphenyl-silanyloxy)-4,7-dihydro-indane (110)



110

In a flame dried flask kept under a stream of nitrogen, was added 4,7-dihydro-2-indanol (**109**, 4 g; 29.41 mmol) in anhydrous dichloromethan (100 mL) and the mixture was stirred for a few min. DMAP (359 mg, 2.94 mmol) and imidazole (4.40 g, 64.70 mmol) were added and the mixture cooled to 0 °C with an ice bath. TBDPSCl (8.892 g, 32.35 mmol) dissolved in dichloromethan (10 mL) was then added dropwise at 0 °C with stirring. After complete addition, the mixture was stirred further for 3 h at room temperature, the solvent evaporated, and the product purified by passing through a small column of silica gel with pentane to provide 10 g (90 %) of pure **110** as colourless viscous oil.

R_F (SiO_2; pentane) = 0.2

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.11 (s, 9 H, ^{tert}-butyl-H), 2.43-2.45 (m, 4 H, 1 / 3-H), 2.60-2.67 (m, 4 H, 4 / 7-H), 4.61-4.64 (m, 1 H, 2-H), 5.77 (s, 2 H, 5 / 6-H), 7.42-7.47 (m, 6 H, 10-12 / 10a-12a-H), 7.73-7.75 (dd, $^3J_1$ = 7.85 Hz, $^4J_2$ = 1.57 Hz, 4 H, 9, 13 / 9a-13a-H).

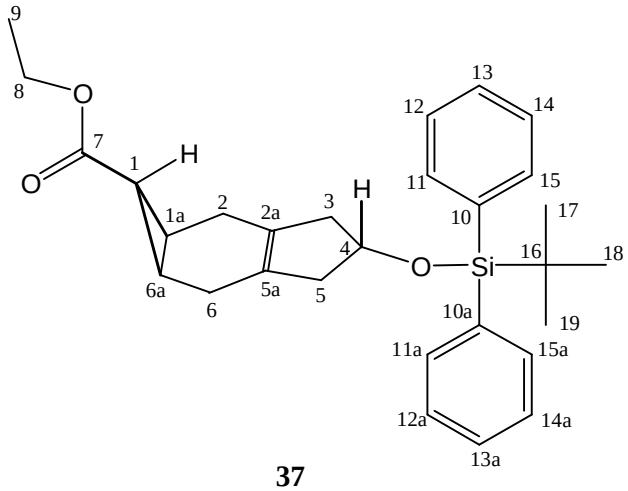
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.11 (s, ^{tert}-butyl), 26.91 (q, ^{tert}-butyl), 27.18 (t, C-4 / 7), 45.45 (t, C-1 / 3), 72.32 (d, C-2), 124.56 (d, C-5 / 6), 127.49 (d, C-10, 12 / 10a, 12a), 129.39 (s, C-3a / 7a), 129.44 (d, C-11 / 11a), 134.59 (s, C-8 / 8a), 135.71 (d, C-9, 13 / 9a, 13a).

IR (film): $\tilde{\nu}$ = 2930 cm^{-1}, 2885, 2856 (s, CH-stretching), 1428 (m), 111 (m), 1074 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (4.73), 204 (4.44), 214 (4.24), 224 (4.09), 256 (2.92), 266 (2.99).

MS (EI, 70 eV): *m/z* (%) = 317 [M^+-^{t}butyl] (91), 240 [317-C_6H_5] (10), 239 [240-H] (52), 227 [240-CH] (99), 199 [239-C_3H_4] (100), 135 [M^+-TBDPS] (10).

4.2.32. 4-(tert-Butyl-diphenyl-silanyloxy)-1,1a,2,3,4,5,6,6a-octahydro-cyclopropa [*f*] indene-1-carboxylic acid ethyl ester (37)



37

To a refluxing mixture of **110** (6.5 g, 17.37 mmol), $CuSO_4$ (anhydrous, 1.45 g) and cyclohexane (anhydrous, 60 mL) was added dropwise with stirring over a 5 h period, a solution of ethyl diazoacetate (6.73 g, 58.99 mmol) in 30 mL of anhydrous cyclohexane with a dropping funnel. The mixture was refluxed for further 60 min and filtered to remove $CuSO_4$. The solution was concentrated and the product was separated by column chromatography on silica gel using pentane as the solvent increasing its polarity with dichloromethane (1-10%). Some unreacted starting material was recovered as it eluted from the column first, followed by the product (6.0 g, 75 %) and by diethyl fumerate as a side product. The product was obtained as colourless viscous oil.

R_F (SiO_2; pentane/CH_2Cl_2; 3:2) = 0.6

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.07 (s, 9H, ^{t}butyl), 1.22-1.24 (t, ^3J = 7.1 Hz, 3 H, 9-H), 2.26-2.35 (m, 4 H, 1 / 3-H), 1.33-1.47 (m, 3 H, 1, 1a, 6a-H), 2.40-2.49 (m, 4 H, 4 / 6-H), 4.16-4.19 (q, ^3J = 7.0, 2 H, 8-H), 4.50-4.52 (m, 1 H, 4-H), 7.69-7.41 (m, 10 H, aromatic rings).

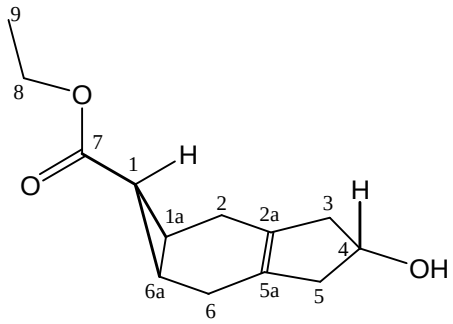
^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.26 (q, C-9), 19.06 (s, ^{t}butyl), 26.89 (q, $(-CH_3)_3$), 21.88 (d, C-1a / 6a), 23.44 (d, C-1), 23.78 (t, C-2 / 6), 45.68 (t, C-3 / 5), 60.26 (t, C-8), 71.90 (d, C-4), 127.50 (d, C-12, 14 / 12a, 14a), 127.53 (d, C-13 / 13a), 135.65 (d, C-11, 15 / 11a, 15a), 135.58 (s, C-10 / 10a), 129.45 (s, C-2a / 5a), 175.02 (s, C-7).

IR (film): $\tilde{\nu}$ = 3071 cm^{-1}, 3049 (m, CH-stretching), 2959, 2930, 2898, 2875, 2858 (s, CH-aromatic), 1723 (s, C=O), 1463, 1428 (m), 1287, 1173, 112, 1076 (s), 1063 (s).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 194 nm (4.96), 208 (4.46), 214 (4.33), 222 (4.22), 228 (3.92), 266 (2.86).

MS (EI, 70 eV): *m/z* (%) = 460 [M^+] (25), 459 [M^+-H] (36), 445 [M^+-CH_3] (95), 403 [M^+-^{t}But] (8), 326 [403-C_6H_5] (1), 297 [326-C_2H_5] (2), 199 [$C_{13}H_{11}O_2$] (100), 183 [199-O] (29).

4.2.33. 4-hydroxy-1, 1a, 2, 3, 4, 5, 6, 6a-octahydro-cyclopropa[*f*]indene-1-carboxylic acid ethyl ester (119)



119

In a 1 L three-necked flask compound **111** (12.5 g, 27.13 mmol) was dissolved in 650 mL of dry THF. The solution was cooled to –78 °C with an acetone-liquid nitrogen bath and tetrabutylammoniumfluoride (TBAF) (68 mL 68.00 mmol) was added in one portion. Cooling was removed and the solution was let to stir for 4 h at room temperature. When the reaction was complete, 200 mL of saturated NH_4Cl-solution was added. The THF was evaporated and the resulting mixture extracted thrice with ethyl acetate. The combined organic phase was washed three times with brine, dried with $MgSO_4$ and the solvent was evaporated to give the crude product. The new material was purified by using silica gel column chromatography with a mixture of ether and pentane (1:3). When all the impurities had emerged from the column, the column was washed with ether to yield the desired product in 96.7 % (5.83 g) yield. The product was isolated as a colorless liquid, which solidified in the refrigerator.

R_F (ether/pentane; 1:1) = 0.26

M. p. = 44 °C

^{1}H NMR (200.1 MHz , $CDCl_3$): δ = 4.42 (m, 1 H, 4-H), 4.09 (q, ^3J = 7.14 Hz, 2 H, 8-H), 2.32 (br. s, 4 H, 1 / 3-H), 1.74 (br.s., 4 H, 2 / 6-H), 1.42 (t, $^3J_1$ = 4.34 Hz, 1 H, 1-H), 1.23 (t, ^3J = 7.14 Hz, 3 H, 9-H), 1.15-1.21 (m, 2 H, 1a / 6a-H).

^{13}C NMR (50.3 MHz , $CDCl_3$): δ = 175.1 (s, C-7), 127.6 (s, C-2a / 5a), 70.2 (d, C-4), 60.3 (t, C-8), 45.9 (t, C-3 / 5), 24.0 (t, C-2 / 6), 23.4 (d, C-1), 21.9 (d, C-1a / 6a), 14.3 (q, C-9).

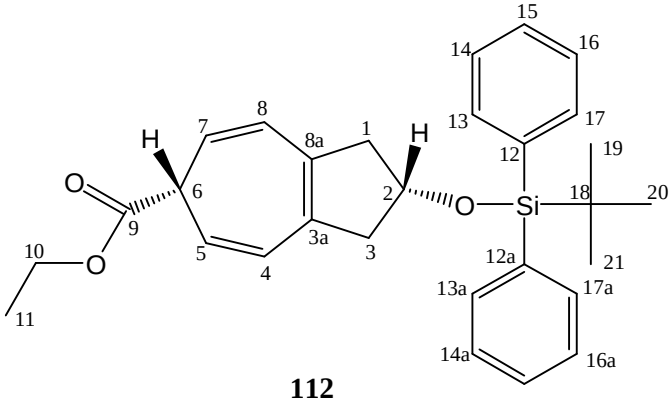
IR (KBr): $\tilde{\nu}$ = 3415 cm^{-1} (m, -OH), 2983 (w), 2899 (m), 2834 (w), 1720 (C=O, s), 1288 (m), 1179 (s), 1040 (w).

UV/Vis (CH_3CN): λ_{max} (lg ε): 192 nm (4.17), 202 (3.86), 212 (3.46), 230 (2.61).

MS (EI, 70 eV): *m/z* (%) = 222 [M^+] (0.8), 204 [M^+-H_2O] (25), 185 (62), 176 [204–CH_3CH_2] (30), 159 [204–EtO] (19), 157 (42), 141 (31), 132 [204–EtOOC] (82), 129 (76), 117 (100), 101 (65).

Elemental analysis $C_{13}H_{18}O_3$ (222): Calcd. C 70.24 %, H 8.16 %; found C 70.01 %, H 8.12 %.

4.2.34. Ethyl 2-(tert-butyl-diphenyl-silanyloxy)-1, 2, 3, 6-tetrahydro-6-azulen-carboxylate (112)



112

Reactant **111** (6.0 g, 13.39 mmol) was dissolved in CCl_4 (300 mL) and the mixture cooled with an ice bath under stirring. Bromine (2.139 g; 13.39 mmol) dissolved in CCl_4 (20 mL) was added dropwise with stirring. When the addition was complete, triethylamine (6.62 g; 65.64 mmol) was added. Triethylamine hydrobromide began to form immediately. The mixture was refluxed for 18 h. The HBr salt was filtered off and the solvent was evaporated. The resulting oil was washed with water and dried with $MgSO_4$ and filtered to get the crude product (5 g) containing ethyl 1,3-dibromo-6-azulenecarboxylate and ethyl 2-(tert-butyl-diphenyl-silanyloxy)-1,2,3,6-tetrahydro-6-azulenecarboxylate. The mixture was purified by column chromatography on silica gel using pentane as an eluent increasing its polarity with dichloromethan (1-10 %). Ethyl 1,3-dibromo-6-azulenecarboxylate **113** (0.5 g, 10 %) being less polar, eluted first (dark blue material) followed by ethyl 2-(tert-butyl-diphenyl-silanyloxy)-1,2,3,6-tetrahydro-6-azulenecarboxylate (**112**, 3.2 g, 52 %, bluish oil).

R_F (SiO_2; pentane/dichloromethane; 3:2 = 0.7

B. p. = > 200 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.98 (s, 9 H, $^{t-}$butyl), 1.24 (t, ^3J = 7.1 Hz, 3 H, 11-H), 2.53 (t, ^3J = 5.6 Hz, 1 H, 6-H), 2.71 (m, 4 H, 1 / 3-H), 4.15-4.19 (q, ^3J = 7.1 Hz, 2 H, 10-H), 4.45-4.54 (m, 1 H, 2-H), 5.19-5.24 (m, 2 H, 5 / 7-H), 6.04-6.08 (2 x d, ^3J = 9.4 Hz, 4 / 8-H), 7.08-7.28 (m, 6 H, 14-16 / 14a-16a-H), 7.49-7.52 (m, 4 H, 13, 17 / 13a, 17a-H).

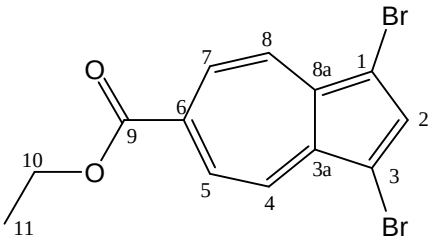
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.20 (q, C-11), 19.08 (s, $^{t-}$Butyl), 26.87 (q, $(-CH_3)_3$), 45.06 (d, C-6), 45.73 (t, C-1 / 3), 60.99 (t, C-10), 72.73 (d, C-2), 117.13 (d, C-5 / 7), 125.07 (d, C-15 / 15a), 127.57 (d, C-14, 16 / 14a, 16a), 129.57 (d, C-4 / 8), 134.29 (s, C-3a / 8a), 135.67 (d, C-13, 17 / 13a, 17a), 139.52 (s, C-12 / 12a), 173.08 (s, C-9).

IR (film): $\tilde{\nu}$ = 2959 cm^{-1}, 2932 (w, CH-stretching), 1737 (s, C=O), 1428 (m), 1199, 1161, 1111, 1086 (m), 702 (s).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (4.91), 266 (3.75), 202 (4.79), 296 (3.46), 312 (3.27).

MS (EI, 70 eV): *m/z* (%) = 458 [M^+] (10), 429 [M^+-C_2H_5] (1.6), 401 [M^+-$^{t-}$But.] (58), 385 [M^+-$C_3H_5O_2$] (98), 323 [401-C_6H_6] (30), 295 [323-C_2H_4] (8), 199 [$C_{13}H_{11}O_2$] (100).

4.2.35. Ethyl 1, 3-dibromo-6-azulen-carboxylate (113)



113

R_F (SiO_2; pentane/dichloromethane; 8:2 = 0.7

M. p. = 115-116 °C

^{1}H NMR (400.1 MHz, CDCl3): δ = 1.37-1-40 (t, ^3J = 7.12 Hz, 3 H, 11-H), 4.36-4-41 (q, ^3J = 7.12 Hz, 2 H, 10-H), 7.83 (s, 1 H, 2-H), 8.01-8.28 (AB q, ^3J = 10.30 Hz, 4 H, 4, 8 / 5, 7-H).

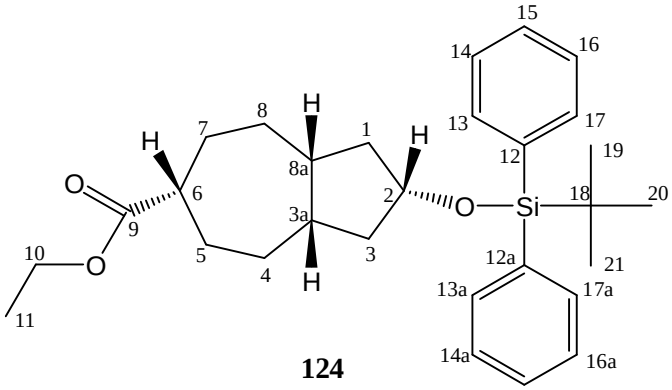
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.25 (q, C-11), 76.68 (t, C-10), 103.86 (2 x s, C-1 / 3), 124.18 (d, C-5 / 7), 135.14 (d, C-4 / 8), 136.87 (2 x s, C-3a / 8a), 138.98 (s, C-6), 140.81 (d, C-2), 167.26 (s, C-9).

IR (KBr): $\tilde{\nu}$ = 2991 cm^{-1}, 2974 (w, CH-stretching), 1721 (s, C=O), 1480, 1386 (m, C=C stretching), 1292, 1270 (s), 1211 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 206 nm (4.27), 222 (4.32), 246 (4.28), 298 (4.81), 344 (3.74), 358 (3.84), 366 (3.32).

MS (EI, 70 eV): *m/z* (%) = 458 [M^+] (87), 330 [M^+-C_2H_4] (100), 313 [M^+-C_2H_5O] (4), 285 [M^+-$C_3H_5O_2$] (10), 206 [285-Br] (29).

4.2.36. Ethyl 2-(tert-butyl-diphenyl-silanyloxy)-decahydro-6-azulen-carboxylate (124)



124

In a 250 mL round bottomed flask were placed **112** (500 mg, 1.09 mmol), dissolved in 50 mL of EtOAc, 250 mg of Pd/C and 3 mL of Et_3N. The mixture was hydrogenated in a hydrogenation apparatus until the consumption of hydrogen stopped. The resulting lightly yellow solution was passed through a pad of silica to remove the Pd/C. The mixture was eluted with 1M HCl to remove the triethylamine. Finally the mixture was washed with water and dried with $MgSO_4$. The solvent was evaporated and the resulting yellow liquid purified by silica gel column chromatography (CH_2Cl_2) yielding a colorless liquid in 93 % (470 mg) yield.

R_F (1:2, CH_2Cl_2/pentane) = 0.41

B. p. = >250 °C / 10 torr

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.68-7.31 (m, 10 H, Ar-*H*), 4.05-4.16 (q, ^3J = 7.14 Hz, 2 H, 10-H), 2.39-2.42 (m, 1 H, 6-H), 3.79-3.83 (m, 1 H, 2-H), 2.14-2.31 (m, 4 H, 1 / 3-H), 1.37-2.03 (m, 10 H, 4, 8 / 5, 7-H), 1.24 (t, ^3J = 7.11 Hz, 3 H, 11-H), 1.02 (s, 9 H, (C*H*$_3$)$_3$C).

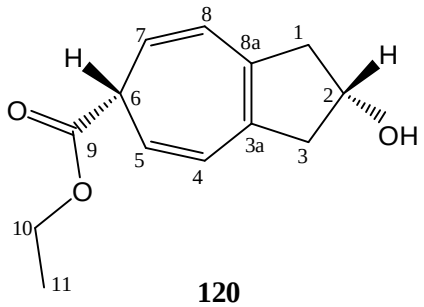
^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 178 (s, C-9), 135.6 (d, C-13, 17 / 13a, 17a), 134.2 (s, C-12, 12a), 129.4 (d, C-14, 16 / 14a, 16a), 127.4 (d, C-15 / 15a), 72.6 (d, C-2), 60.1 (t, C-10), 46.1 (d, C-6), 43.88 (d, C-3a / 8a), 32.99 (t, C-1 / 3), 29.41 (t, C-4 / 8), 26.86 (t, C-5 / 7), 26.9 (q, (*C*H$_3$)$_3$C), 19.1 (s, C-18), 14.3 (q, C-11).

UV/Vis (CH_3CN): λ_{max} (lg ε): 194 nm (4.78), 212 (4.25), 222 (4.13), 260 (2.86), 266 (2.88).

IR (film): $\tilde{\nu}$ = 3072 cm^{-1} (w), 2929 (s), 2856 (s), 1732 (s), 1473 (m), 1428 (m), 1288 (m), 1162 (s), 1112 (s), 1085 (m).

MS (EI, 70 eV): *m/z* (%) = 285 [M$^+$-^{t}Bu–Ph–CH_3CH_2O] (54), 257 [285–CO] (18), 229 (14), 227 (20), 199 [$C_{13}H_{11}O_2$] (100), 153 [199-C_2H_5OH] (10), 105 [Ph-Si] (8).

4.2.37. 2-Hydroxy-1,2,3,6-tetrahydro-azulen-6-carboxylic acid ethyl ester (120)



120

4-hydroxy-1,1a,2,3,4,5,6,6a-octahydro-cyclopropa[*f*]indene-1-carboxylic acid ethyl ester **119** (9.7 g, 43.64 mmol) was dissolved in 500 mL of CCl_4 and the mixture cooled with an ice bath. Bromine (0.222 mL, 4.34 mmol) in 40 mL of CCl_4 was added dropwise with stirring. When the addition was complete, triethylamine (30.4 mL, 0.217 mol) was added. The ice-bath was removed and the mixture was refluxed for 18 h. The HBr salt was filtered off and the filtrate was evaporated. The resulting oil was partitioned between ether and dilute aqueous acid (HCl). The ether layer was washed with water and dried with $MgSO_4$. The ether was evaporated and the product purified by silica gel column chromatography using a 1:1 solution of ether and pentane as the eluent. First to elute was the intense blue by-product (1, 3-dibromo azulene-6-carboxylic acid ethyl ester) and then the product was isolated as a viscous brown liquid/paste in 62 % (5.96 g) yield. Further purification with a silica gel PTLC-plate yielded a light yellow viscous liquid.

R_F (ether/pentane; 3:2) = 0.32

B. p. = 139-142 °C / 5 torr (distillation of a colorless liquid begins but at the same time visible decomposition of the product can be observed).

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 6.23 (d, ^3J = 9.26 Hz, 2 H, 4 / 8-H), 5.42 (m, 2 H, 5 / 7-H), 4.54 (m, 1 H, 2-H), 4.24 (q, ^3J = 7.15 Hz, 2 H, 10-H), 3.06 / 2.72 (m, 4 H, 1 / 3-H), 2.60 (m, 1 H, 6-H), 1.30 (t, ^3J = 7.14 Hz, 3 H, 11-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 173.0 (s, C-9), 139.3 (s, C-3a / 8a), 125.00 (d, C-4 / 8), 117.01 (d, C-5 / 7), 70.84 (d, C-2), 61.01 (t, C-10), 45.05 (d, C-6), 46.36 (t, C-1 / 3), 14.2 (q, C-11).

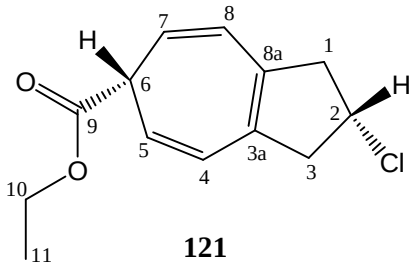
IR (film): $\tilde{\nu}$ = 3427 cm^{-1} (m), 2980, 2930, 2907 (m, CH-stretching), 1736 (s, C=O), 1368 (m), 1297 (m), 1263 (m), 1194 (m), 1174 (m), 1040 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 194 nm (4.00), 206 (4.10), 274 (3.43), 294 (3.18), 310 (2.84), 330 (2.44).

MS (EI, 70 eV): *m/z* (%) = 220 [M^+] (12), 211 (3), 200 (3), 191 [M^+-CH_3CH_2] (4), 173 [191-H_2O] (9), 147 [M^+-EtOOC] (100), 129 [147–H_2O] (49), 115 (11).

HRMS ($C_{13}H_{16}O_3$): Calcd. 220.1099; found 220.10964 ± 4 ppm.

4.2.38. 2-Chloro-1,2,3,6-tetrahydro-azulen-6-carboxylic acid ethyl ester (121)



121

In a 50 mL three-necked flask was placed alcohol **120** (100 mg, 0.45 mmol) dissolved in 10 mL of CCl_4. Then Ph_3P (132 mg, 1.1 eq) was added and the mixture was refluxed overnight. When the reaction was complete the mixture was filtered to remove unreacted Ph_3P. The product was purified by silica gel column chromatography using a mixture of CH_2Cl_2 and pentane (1:3) as the eluent. The first compound to elute was unreacted Ph_3P then the product started eluting. The last fraction to emerge was unreacted starting material. The product was isolated as a light bluish liquid in 60 % (64.5 mg) yield.

R_F (CH_2Cl_2) = 0.73

B. p. = 120-123 °C / 5 torr

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 6.22 (m, 2 H, 4 / 8-H), 5.47 (m, 2 H, 5 / 7-H), 4.60 (m, 1 H, 2-H), 4.25 (q, ^3J = 7.14 Hz, 2 H, 10-H), 3.01-3.32 (m, 4 H, 1 / 3-H), 2.68 (m, 1 H, 6-H), 1.30 (t, ^3J = 7.14 Hz, 3 H, 11-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 173.0 (s, C-9), 134.8 (s, C-3a / 8a), 124.4 (d, C-4 / 8), 117.5 (d, C-5 / 7), 61.2 (t, C-10), 47.1 (t, C-1 / 3), 45.1 (d, C-2), 44.2 (d, C-6), 14.2 (q, C-11).

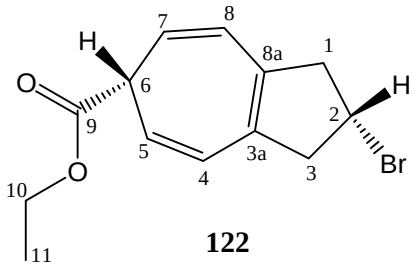
IR (film): $\tilde{\nu}$ = 3450 cm^{-1} (w), 3026 (w), 2981 (m), 2938 (m), 2906 (w), 2852 (w), 1737 (s), 1368 (m), 1303 (s), 1258 (s), 1196 (s), 1176 (s), 1166 (m), 1117 (w), 751 (w), 712 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε): 206 nm (4.26), 272 (3.56).

MS (EI, 70 eV): *m/z* (%) = 240 [M^+(^{37}Cl)] (3), 238 [M^+(^{35}Cl)] (7), 212 [M^+-HCl] (1), 209 [$^{35}M^+$-CH_3CH_2] (6), 200 (6), 173 [M^+-CH_3CH_2–HCl] (8), 167 [$^{37}M^+$-EtOOC] (29), 165 [$^{35}M^+$-EtOOC] (100), 129 [167/165–HCl] (86).

Elemental analysis $C_{13}H_{15}O_2Cl$ (238.71): Calcd. C 65.41 %, H 6.33 %; found C 65.52 %, H 6.27 %.

4.2.39. 2-Bromo-1,2,3,6-tetrahydro-azulen-6-carboxylic acid ethyl ester (122)



122

In a 250 mL three-necked flask PPh_3 (1.25 g, 4.77 mmol) was dissolved in 50 mL of CCl_4 under nitrogen. The solution was cooled with an ice-bath and from a dropping funnel Br_2 (762 mg, 4.77 mmol) in 20 mL of CCl_4 was added dropwise to the solution. When the addition was complete the ice-bath was removed and the mixture was left to stir at room temperature. After 15 min alcohol **120** (1.0 g, 4.54 mmol) in 20 mL of CCl_4 was added from a dropping funnel in one portion. When the addition was complete the mixture was refluxed for 1 h. Water was added and the organic layer was extracted with diethyl ether. The organic layer was again washed with water, separated and dried with $MgSO_4$. The solvent was evaporated and the product purified by silica gel column chromatography using a mixture of CH_2Cl_2 and pentane as the eluent. The purification yielded 390 mg (30 %) of the product as a light blue liquid.

R_F (CH_2Cl_2/pentane; 1:1) = 0.6

B. p. = 134-136 °C / 5 torr (distilled as a colorless liquid but also visibly decomposed simultaneously.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 6.17 (m, 2 H, 4 / 8-H), 5.40 (m, 2 H, 5 / 7-H), 4.57 (m, 1 H, 2-H), 4.19 (q, ^3J = 7.14 Hz, 2 H, 10-H), 3.36-3.02 (m, 4 H, 1 / 3-H), 2.68 (t, ^3J = 5.63 Hz, 1 H, 6-H), 1.24 (t, ^3J = 7.13 Hz, 3 H, 11-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 173.2 (s, C-9), 139.1 (s, C-3a / 8a), 124.3 (d, C-4 / 8), 118.1 (d, C-5 / 7), 61.1 (t, C-10), 47.8 (t, C-1 / 3), 47.5 (d, C-6), 45.1 (d, C-2), 14.2 (q, C-11).

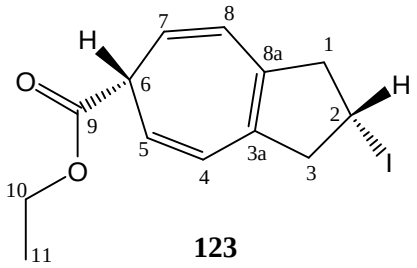
IR (film): $\tilde{\nu}$ = 3452 cm^{-1} (w), 3025 (w), 2980, 2938 (m, CH-stretching), 2873, 2824 (w), 1736 (s, C=O), 1368 (m), 1302 (s), 1226 (s), 1196 (s), 1173 (s), 1040 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε): 206 nm (4.31), 270 (3.55), 312 (2.79), 320 (2.69), 340 (2.60).

MS (EI, 70 eV): *m/z* (%) = 284 [(^{81}Br)M^+] (2), 282 [(^{79}Br)M^+] (2), 253 [$^{79}M^+$-CH_3CH_2] (1), 211 [$^{81}M^+$-EtOOC] (26), 209 [$^{79}M^+$-EtOOC] (26), 202 [M^+-HBr] (12), 185(12), 172 [M^+-HBr–CH_3CH_2] (14), 129 [M^+-EtOOC–HBr] (100).

Elemental analysis $C_{13}H_{15}O_2Br$ (283.16): Calcd. C 55.14 %, H 5.34 %; found C 55.46 %, H 5.44 %.

4.2.40. 2-Iodo-1,2,3,6-tetrahydro-azulen-6-carboxylic acid ethyl ester (123)



123

To a mixture of alcohol **120** (200 mg, 0.91 mmol), PPh_3 (476 mg, 1.82 mmol) and hexamethylphosphorous triamide (651 mg, 3.63 mmol) in 10 mL of iodo-benzene (461 mg, 1.82 mmol) were added in one portion. The dark mixture was stirred at room temperature for 5 h until TLC analysis showed consumption of all starting material. The mixture was diluted with ether (40 mL) and quenched with ice-cold saturated solution of sodium bicarbonate. The organic layer was separated and washed consecutively with 1M H_2SO_4, water and finally with a saturated solution of $NaHCO_3$. The organic phase was dried with $MgSO_4$. The product was purified by silica gel column chromatography using a mixture of CH_2Cl_2 and pentane (1:2) as the eluent. The product was isolated as a colourless liquid (180 mg) in 60 % yield. The product can be preserved for a few days in the deepfreeze but the colourless liquid turns gradually dark brown, decomposing.

R_F (CH_2Cl_2/pentane; 1:2) = 0.42

B. p. = decomposed on heating

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 6.22 (m, 2 H, 4 / 8-H), 5.43 (m, 2 H, 5 / 7-H), 4.76 (m, 1 H, 2-H), 4.25 (q, ^3J = 7.16 Hz, 2 H, 10-H), 3.38-3.12 (m, 4 H, 1 / 3-H), 2.74 (t, ^3J = 5.58 Hz, 1 H, 6-H), 1.30 (t, ^3J = 7.13 Hz, 3 H, 11-H).

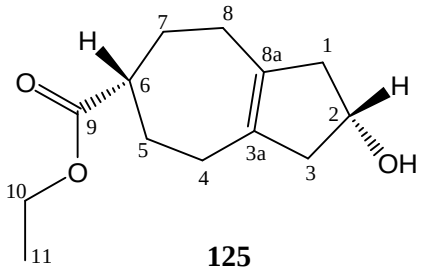
^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 173.0 (s, C-9), 134.8 (s, C-3a / 8a), 124.3 (d, C-4 / 8), 118.0 (d, C-5 / 7), 61.1 (t, C-10), 49.8 (t, C-1 / 3), 49.9 (d, C-6), 45.1 (d, C-2), 14.2 (q, C-11).

UV/Vis (CH_3CN): λ_{max} (lg ε): 198 nm (4.32), 264 (3.60).

MS (EI, 70 eV): *m/z* (%) = 330 [M^+] (0.5), 257 [M^+-EtOOC] (4), 202 [M^+-HI] (13), 173 [202–CH_3CH_2] (6), 129 [M^+-HI–EtOOC] (100).

Elemental analysis $C_{13}H_{15}O_2I$ (330.17): Calcd. C 47.29 %, H 4.58 %; found C 47.68 %, H 4.57 %.

4.2.41. 2-Hydroxy-1,2,3,4,5,6,7,8-octahydro-azulen-6-carboxylic acid ethyl ester (125)



125

In a 250 mL round-bottomed flask were placed 2-hydroxy-1,2,3,6-tetrahydro-azulene-6-carboxylic acid ethyl ester **120** (1.35 g, 6.13 mmol), dissolved in 100 mL of THF, 1.0 g of Pd/C and 15 mL of Et_3N. The mixture was hydrogenated in a hydrogenation apparatus until the consumption of hydrogen ceased. The resulting solution was passed through a pad of silica to remove the Pd/C. The THF was evaporated, 100 mL of EtOAc was added and the mixture was extracted with 1M HCl to remove triethylamine. Finally the mixture was washed with water and dried with $MgSO_4$. The solvent was evaporated and the resulting yellow liquid purified by silica gel column chromatography (CH_2Cl_2) yielding **125** as a lightly yellow liquid in 93 % (1.28 g).

R_F (EtOAc/pentane; 1:2) = 0.39

B. p. = 133-135 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.39 (m, 1 H, 2-H), 4.05 (q, ^3J = 7.14 Hz, 2 H, 10-H), 2.47-1.75 (m, 8 H, 1 / 3-H, 4 / 8-H), 1.75-1.26 (m, 4 H, 5 / 7-H), 1.70 (br. s., 1 H, 6-H), 1.18 (t, ^3J = 7.11 Hz, 3 H, 11-H).

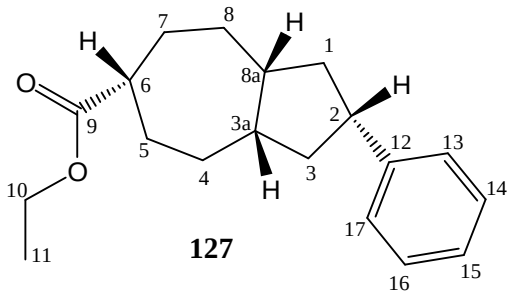
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 174.8 (s, C-9), 127.7 (s, C-3a / 8a), 70.3 (d, C-2), 60.3 (t, C-10), 46.0 (t, C-1 / 3), 24.1 (t, C-4 / 8), 23.5 (d, C-6), 22.0 (t, C-5 / 7).

UV/Vis (CH_3CN): λ_{max} (lg ε): 192 nm (3.91), 276 (2.36), 294 (2.29), 324 (2.19), 364 (2.07).

IR (film): $\tilde{\nu}$ = 3416 cm^{-1} (m), 2980, 2927 (s, CH-stretching), 2838 (m), 1727 (s, C=O), 1445 (m), 1368 (m), 1289 (s), 1234 (m), 1216 (m), 1175 (s), 1061 (m), 1039 (m).

MS (70 eV): *m/z* (%) = 224 [M^+] (8), 206 [M^+-H_2O] (23), 178 [206–CH_2CH_2] (68), 162 [206–EtO] (21), 150 [178-CO] (21), 132 [178-HCOOH] (55), 105 [132-C_2H_3] (38), 91 [105-CH_2] (100), 79 [105-C_2H_2] (54).

4.2.42. 2-Phenyl-decahydro-azulen-6-carboxylic acid ethyl ester (127)



127

In a 50 mL three-necked flask the alcohol **126** (40 mg, 0.179 mmol), dissolved in 3 mL of benzene, was placed. The mixture was cooled with an ice-bath and $AlCl_3$ (60.5 mg, 0.454 mmol) was added in one portion. The ice-bath was removed and the mixture was warmed to 50-60 °C and stirred for 4-5 h. When the reaction was complete, the mixture was cooled to room temperature and water was added, and the mixture was extracted first with 50 mL of Et_2O then the organic layer was washed first with 1N HCl and finally with water. The organic phase was dried with $MgSO_4$. The solvent was evaporated and the product was purified with silica gel PTLC using CH_2Cl_2 and pentane (1:3) as the eluent system yielding 20 mg (38 %) of the product as clear liquid.

R_F (dichloromethane/pentane; 1:3) = 0.6

B. p. = Could not be taken due to lack of material.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.0-7.3 (m, 5 H, Ar-*H*), 4.09 (q, ^3J = 7.13 Hz, 2 H, 10-H), 1.25-3.30 (m, 16 H, protons of both rings), 1.21 (t, ^3J = 7.0 Hz, 3 H, 11-H).

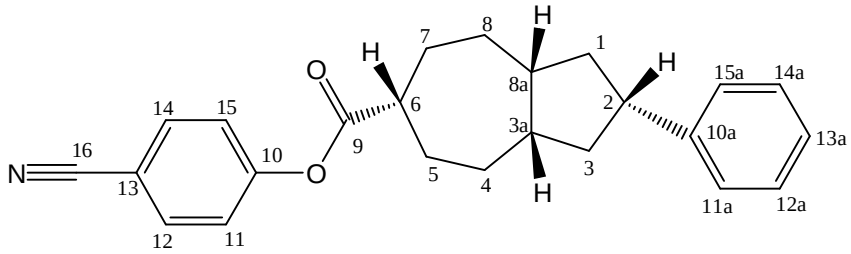
^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 177.3 (s, C-9), 128.8 (d, C-14 / 16), 128.1 (s, C-12), 127.0 (d, C-13 / 17), 126.1 (d, C-15), 60.2 (t, C-10), 45.2 (d, C-2), 44.2 (d, C-6), 42.6 (d, C-3a / 8a), 36.9 (t, C-1 / 3), 33.8 (t, C-4 / 8), 26.8 (t, C-5 / 7), 14.2 (q, C-11).

IR (film): $\tilde{\nu}$ = 3060 cm^{-1} (w, CH-stretching), 2927 (s, CH-stretching), 2855 (m), 1731 (s, C=O), 1448 (m), 1264 (w), 1194 (m), 1174 (m), 755 (m), 699 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 194 nm (4.62), 204 (4.19), 210 (4.11), 218 (3.96), 226 (3.57), 260 (3.46), 290 (3.07), 319 (3.00).

MS (70 eV): *m/z* (%) = 286 [M^+] (100), 284 [M^+-H_2] (44), 257 [M^+-CH_3CH_2] (10), 240 [M^+-HCOOH] (33), 209 [M^+-C_6H_5] (14), 210 [240-C_2H_6] (47), 183 [210-C_2H_3] (20), 169 [183-CH_2] (48), 156 [169-CH] (35), 143 [169-C_2H_2] (63).

4.2.43. 2-Phenyl-decahydro-azulen-6-carboxylic acid 4-cyano-phenyl ester (128)



128

In a 50 mL three-necked flask the ester **127** (70 mg, 0.244 mmol) and 20 mL of CH_2Cl_2 were placed. BBr_3 (0.25 mL, 0.25 mmol) was added in one portion. The reaction mixture turned dark brown and it was left stirring at 50 °C for 4-5 h and then *p*-cyanophenol (120 mg, 1.01 mmol) was added in one portion and the mixture was left to stir for further 2 h. The solvent was evaporated, water was added and the mixture was extracted twice with EtOAc. The organic layer was dried with $MgSO_4$, the solvent was evaporated and the resulting residue purified with silica gel PTLC using a mixture of CH_2Cl_2: pentane (1:1) as the eluent to yield 18 mg (20%) of the product as a light yellow liquid.

R_F (CH_2Cl_2/pentane; 1:1) = 0.38

B. p. = 270-275 °C / 5 torr

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.58-7.61 (m, 2 H, 12 / 14-H), 7.08-7.21 (m, 7 H, aromatic protons), 3.01-3.07 (m, 1 H, 6-H), 2.45-2.54 (m, 1 H, 2-H), 134-2.08 (m, 14 H, protons of both rings).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 173.53 (s, C-9), 154.21 (s, C-10), 145.63 (s, C-10a), 133.60 (d, C-12 / 14), 128.28 (d, C-12a / 14a), 126.94 (d, C-11a / 15a), 125.86 (d, C-13a), 122.69 (d, C-11 / 15), 118.25 (s, C-16), 109.55 (s, C-13), 45.07 (d, C-6), 43.9 (d, C-2), 41.83 (d, C-3a / 8a), 36.84 (t, C-1 / 3), 32.83 (t, C-4 / 8), 26.15 (t, C-5 / 7).

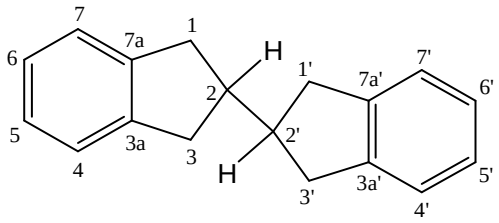
UV/Vis (CH_3CN): λ_{max} (lg ε): 194 nm (4.81), 222 (4.14), 232 (4.21), 256 (3.28), 264 (3.18).

IR (KBr): $\tilde{\nu}$ = 3027 cm^{-1} (w, CH-stretching), 2934 (s, CH-stretching), 2858 (m), 2230 (m, CN), 1758 (s, C=O), 1602 (m), 1504 (m), 1211 (s), 1166 (s), 1115 (s).

MS (EI, 70 eV): *m/z* (%) = 359 [M^+] (6), 257 [M^+-CNC_6H_5] (1), 241 [257–O] (70), 213 [241–C=O] (100), 199 [213-CH_2] (32), 135 [213-C_6H_6] (63), 95 [135-C_3H_4] (28).

HRMS ($C_{24}H_{25}O_2N$): Calcd. 359.18852; found 359.18819 ± 1 ppm

4.2.44. 2,3,2',3'-Tetrahydro-1*H*,1'*H*-[2,2']biindenyl (43)



43

In a dry 500 mL three-necked flask under nitrogen, naphthalene (25.6 g, 0.2 mol) was dissolved in 300 mL of THF. Solid lithium (5.6 g, 0.8 mol) cuttings were added with vigorous stirring and the mixture was stirred for 1 h at room temperature. Then a mixture of ethylene glycol monobutyl ether (53.0 mL, 0.4 mol) and indene (47.4 mL, 0.4 mol) was added dropwise to the solution. After the addition was complete, the mixture was stirred for 2 h. Remaining pieces of lithium were then destroyed by slow addition of methanol. After these lithium pieces were completely destroyed, water was added and the mixture was extracted a few times with ether. The organic layer was separated, dried with $MgSO_4$ and the solvent was evaporated. From the remaining residue unreacted indene was distilled away (approx. 18 g) under vacuum. Finally the product was purified by column chromatography on silica gel eluting with pentane. The compound was separated by silica gel column chromatography with pentane and after separation washed with small amounts of pentane to remove remaining indene. The compound is a colorless solid, which after recrystallization from CH_2Cl_2 and pentane, yielded colorless needles in 33 % (20 g) yield.

R_F (CH_2Cl_2/pentane; 1:5) = 0.81

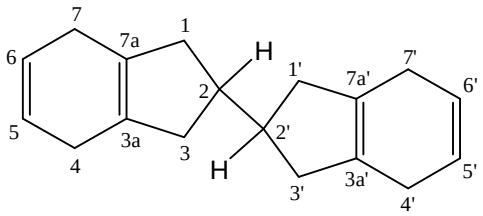
M. p. = 164-166 °C (Lit.[85] 165-166 °C)

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.50-2.60 (m, 2 H, 2 / 2'-H), 2.60-3.15 (m, 8 H, 1, 3 / 1', 3'-H), 7.10-7.21 (m, 8 H, Ar-*H*).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 38.1 (t, C-1 / 3), 45.5 (d, C-2), 124.3 (d, C-5 / 6), 126.1 (d, C-4 / 7), 143.3 (s, C-3a / 7a).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 196 nm (4.96), 206 (4.38), 216 (4.27), 224 (3.65), 260 (3.35), 268 (3.50), 274 (3.51).
IR (KBr): $\tilde{\nu}$ = 3066 cm^{-1} (w), 3016 (w), 2935 (m) , 2898 (m) , 1473 (s) , 747 (s) , 739 (s).
MS (EI, 70 eV): *m/z* (%) = 234 [M^+] (25), 129 [M^+-C_8H_9] (100), 117 [$C_9H_9^+$] (49), 103 [117-CH_2] (20).
Elemental analysis $C_{18}H_{18}$ (234.34): Calcd. C 92.26 %, H 7.74 %; found C 91.91 %, H 7.80 %.

4.2.44. 2, 3,4,7,2',3',4',7'-Octahydro-1*H*, 1'*H*-[2, 2']biindenyl (129)



129

2,3,2',3'-Tetrahydro-1*H*,1'*H*-[2,2']biindenyl **43** (2.4 g, 10.24 mmol) was dissolved in a mixture of dry EtOH (100 mL) and anhydrous THF (300 mL) in a 1 L three-necked flask. The flask was cooled to –78 °C with an acetone-liquid nitrogen bath. Liquid NH_3 (100 mL) was added followed by solid sodium metal vigorous stirring until a blue color persisted for 20 min. The NH_3 was allowed to evaporate overnight. The remaining residue was partitioned between ether and water. The ether layer was evaporated and the resulting residue was partitioned again with ether and water. The ether layer was dried with $MgSO_4$ and the solvent evaporated to give the crude product in 98 % (2.4 g) yield. Since it is rather unstable, the product was not purified, but used readily for further reaction. TLC analysis of the crude product showed the presence of small amounts of starting material, monoreduced product and some unknown by-product.

R_F (CH_2Cl_2/pentane; 1:5) = 0.88
M. p. = 130-134 °C

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.91-2.32 (m, 10 H, cyclopentane ring protons), 2.55 (s, 8 H, 4, 7 / 4', 7'-H), 5.68 (s, 4 H, 5, 6 / 5', 6'-H).

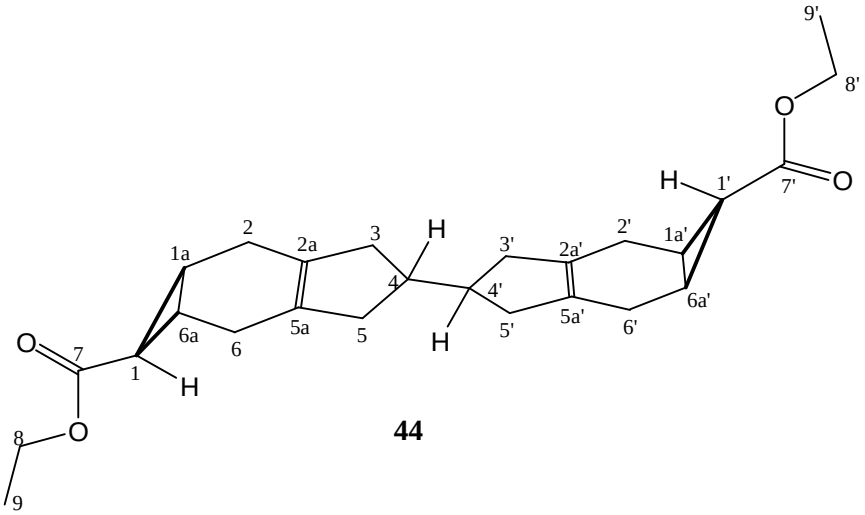
^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 27.5 (t, C-4 / 7), 40.5 (t, C-1 / 3), 41.7 (d, C-2), 124.7 (d, C-5 / 6), 131.1 (s, C-3a / 7a).

UV/Vis (CH_3CN): λ_{max} (lg ε): 194 nm (4.19), 196 (4.19), 208 (3.68), 216 (3.49), 224 (3.03), 268 (2.39), 274 (2.39).

IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (m), 2910 (s), 2896 (s), 2884 (s), 2821 (s), 1640 (w), 1416 (w), 738 (m), 666 (s).

MS (EI, 70eV): *m/z* (%) = 238 [M^+] (15), 236 [M^+-H_2] (21), 119[$C_9H_{11}^+$] (58), 117[$C_9H_9^+$] (100), 91 [C_7H_7] (72).

4.2.45.1,1a,2,3,4,5,6,6a,1',1a',2',3',4',5',6',6a'-Hexadecahydro-[4,4']bi [cyclopropa[*f*]]indenyl]-1, 1'-dicarboxylic acid diethylester (44)



44

To a refluxing mixture of **129** (2.2 g, 9.22 mmol), anhydrous $CuSO_4$ (0.4 g) and anhydrous cyclohexane (300 mL) was added dropwise ethyldiazoacetate (6.5 mL, 30.83 mmol) in cyclohexane (100 mL). After the addition was complete, the mixture was refluxed for further 60 min. The mixture was filtered to remove the $CuSO_4$; the solution was concentrated and purified by silica gel column chromatography (1:2, CH_2Cl_2: pentane). At first some starting material was recovered followed by mono addition product **45** in 10.4 % (306 mg) yield and finally the desired **44** in 12 % (454 mg) yields. The product was washed with small amounts of pentane to remove diethylfumarate formed as a side product.

R_F (CH_2Cl_2/pentane; 2:1) = 0.4

M. p. = 148-151 °C

^{1}H NMR (400.1 MHz , $CDCl_3$): δ = 4.15 (q, ^3J = 7.15 Hz, 2 H, 8-H), 2.32 (br. s, 2 x 4 H, 3 / 5-H), 2.20 (br. s, 2 x 1 H, 4-H), 1.64-1.94 (m, 2 x 4H, 2 / 6-H), 1.39-1.47 (m, 2 x 3 H, 1, 1a, 6a-H), 1.29 (t, ^3J = 7.13 Hz, 2 x 3 H, 9-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 174.99 (s, C-7), 129.17 (s, C-2a / 5a), 60.19 (t, C-8), 41.63 (d, C-4), 40.77 (t, C-3 / 5), 24.16 (t, C-2 / 6), 24.14 (d, C-1), 22.15 (d, C-1a / 6a), 14.29 (q, C-9).

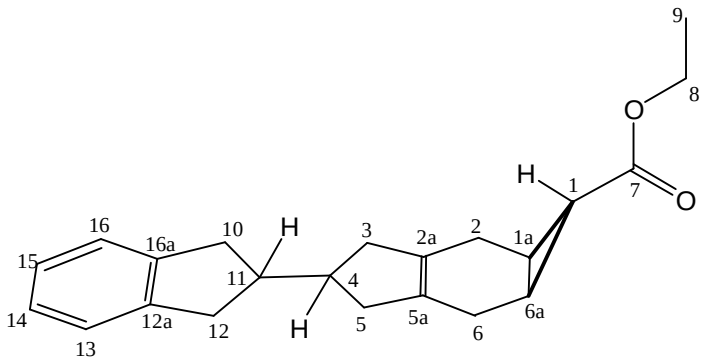
UV/Vis (CH_3CN): λ_{max} (lg ε) = 192 nm (4.35).

IR (KBr): $\tilde{\nu}$ = 3417 cm^{-1} (w), 2990 (w), 2888 (m), 2825 (s), 1719 (s, C=O), 1293 (s), 1180 (s), 810 (m).

MS (EI, 70 eV): *m/z* (%) = 410 [M^+] (24), 365 [M^+-CH_3CH_2O] (28), 336 [365-CO] (9), 323 [336-CH] (85), 291 [336–CH_3CH_2O] (9), 249 [276–CO] (10), 205 [M^+/2] (48), 159 [205–CH_3CH_2O] (89), 131 [205–CH_3CH_2OCO] (100), 117 [131–CH_2] (56).

HRMS $C_{26}H_{34}O_4$ Calcd. 410.2457; found 410.2447 ± 1 ppm

4.2.46. 4-Indan-2-yl-1,1a,2,3,4,5,6,6a-octahydro-cyclopropa[*f*]indene-1-carboxylic acid ethylester (45)



45

The compound **45** was isolated as a colouress powder in 10.4 % (306 mg) yield. The product was washed a few times with pentane to remove the traces of diethylfumarate.

R_F (CH_2Cl_2/pentane; 1:1) = 0.43

M. p. = 98-99 °C

^{1}H NMR (400.1 MHz , $CDCl_3$): δ = 7.23-7.14 (m, 4 H, Ar-*H*), 4.15 (q, ^3J = 7.12 Hz, 2 H, 8-H), 3.03 (dd, $^3J_1$ = 7.81 Hz, $^3J_2$ = 15.58 Hz, 2 H, 3-H), 2.65 (dd, $^3J_1$ = 8.64 Hz, $^3J_2$ = 15.45 Hz,

2 H, 5-H), 1.90-2.49 (m, 10 H, 2, 4, 6, 10, 11, 12-H), 1.80 (br.s., 2 H, 1a / 6a-H), 1.46 (t, ^3J = 4.32 Hz , 1 H, 1-H), 1.30 (t, ^3J = 7.13 Hz, 3 H, 9-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 175.0 (s, C-7), 143.6 (s, C-2a / 5a), 129.2 (s, 12a / 16a), 126.0 (d, C-13 / 16), 124.3 (d, C-14 / 15), 60.2 (t, C-8), 45.8 (d, C-11), 41.0 (d, C-4), 40.9 (t, C-3 / 5), 37.8 (t, C-2 / 6), 24.1 (t, C-10 / 12), 23.3 (d, C-1), 22.1 (d, C-1a / 6a), 14.3 (q, C-9).

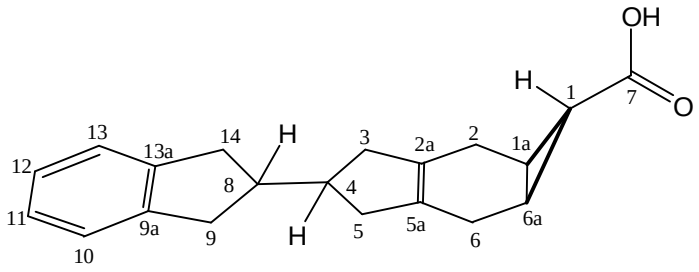
IR (KBr): $\tilde{\nu}$ = 3418 cm^{-1} (w), 2977 (m), 2888 (m), 2828 (m), 1721 (s, C=O), 1291 (m), 1175 (s), 751 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε): 196 nm (4.69), 194 (4.68), 206 (4.12), 214 (3.98), 218 (3.86), 268 (2.96), 274 (2.97).

MS (EI, 70 eV): *m/z* (%) = 324 [M^+] (13), 277 [M^+-EtO] (9), 236 [277-C_2HO] (28), 234 [236-H_2] (59), 205 (29), 159 (19), 143 (19), 131 [M^+-$C_{12}H_{14}O_2$] (67), 117 [$C_9H_9^+$] (100), 91 (98).

Elemental analysis $C_{22}H_{26}O_2$ (322.45): Calcd. C 81.95 %, H 8.13 %; found C 81.97 %, H 8.23 %.

4.2.47. 4-Indan-2-yl-1,1a,2,3,4,5,6,6a-octahydro-cyclopropa[f]indene-1-carboxylic acid (131)



131

In a 100 mL round bottomed flask 20 mL of EtOH and 12 mL of 1M NaOH were placed. The mixture was left to stir for a while and ethyl ester **45** (58 mg, 0.18 mmol) was added, the mixture was heated to 50-60 °C to ensure complete dissolution of the ethyl ester and left to stir for 4-6 h. When TLC analysis showed no more starting material to be present, the mixture was acidified with 1M HCl. Then the EtOH was evaporated and the residual water extracted twice with ethyl acetate and once with CH_2Cl_2. The organic parts were combined, washed with water and dried ($MgSO_4$). The solvent was evaporated and the residue purified by column chromatography on silica gel by first eluting the impurities with CH_2Cl_2 , and

finally washing the column with Et_2O to yield 31 mg (57 %) of the compound as a colourless solid.

R_F (Et_2O/pentane; 1:1): 0.69

M. p = 205-208 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.25-7.09 (m, 4 H, Ar-*H*), 3.01 (dd, $^3J_1$ = 7.56 Hz, $^3J_2$ = 15.76 Hz, 2 H, 3-H), 2.62 (dd, $^3J_1$ = 8.39 Hz, $^3J_2$ = 15.49 Hz, 2 H, 5-H), 1.99-2.43 (m, 10 H, 2, 4, 6, 8, 9, 14-H), 1.83 (br.s., 2 H, 1a / 6a-H), 1.46 (t, ^3J = 4.25 Hz, 1 H, 1-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 180.90 (s, C-7), 143.57 (s, C-2a / 5a), 129.15 (s, 9a / 13a), 126.02 (d, C-10 / 13), 124.35 (d, C-11 / 12), 45.83 (d, C-8), 41.38 (d, C-4), 40.98 (t, C-3 / 5), 40.86 (d, C-1), 37.84 (t, C-2 / 6), 24.13 (t, C-9 / 14), 23.25 (d, C-1a / 6a).

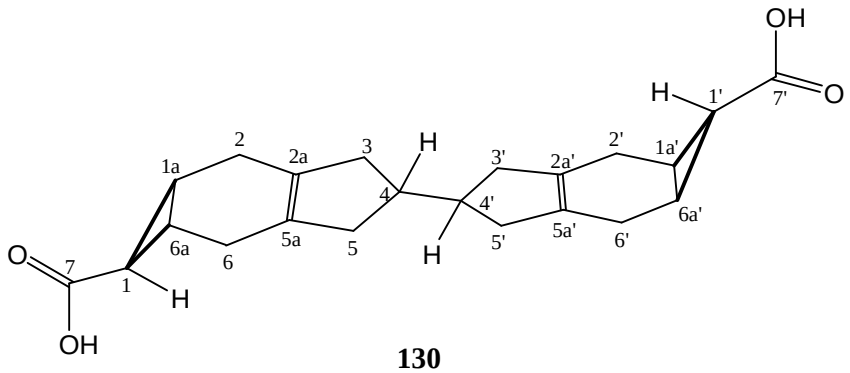
IR (KBr): $\tilde{\nu}$ = 3069 cm^{-1} (w, CH-stretching), 3037, 3027, 3006 (w), 2915 (m), 2878, 2853, 2833 (m), 2723, 2676, 2619, 2581 (w), 1686 (s, C=O), 1655, 1648, 1458, 1439, 1345 (w), 1296 (m), 1221 (w), 1210 (m).

UV/Vis (CH_3CN): λ_{max} (lg ε): 196 nm (4.43), 208 (3.96), 216 (3.72), 222 (3.41), 234 (2.74), 256 (2.73), 268 (2.91), 274 (2.80).

MS (EI, 70 eV): *m/z* (%) = 294 [M^+] (100), 248 [M^+-HCOOH] (5), 177 [M^+-C_9H_9] (83), 131 [177-HCOOH] (90), 116 [C_9H_8] (99).

Elemental analysis $C_{20}H_{22}O_2$ (294.39): Calcd. C 81.60 %, H 7.53 %; found C 81.23 %, H 7.53 %.

4.2.48. 1,2,3,4,5,6,1´,2´,3´,4´,5´,6´-dodecahydro-[4,4´]bi[cyclopropa[f]]indenyl]-1,1´-dicarboxylic acid (130)



130

In a 100 mL round-bottom flask 20 mL of EtOH and 12 mL of 1M NaOH were placed. The mixture was left to stir for a while and then diester **44** (50 mg, 0.12 mmol) was added, the mixture was heated to 50-60 °C to ensure complete dissolution of diester, and left to stir for 4-6 h. When TLC analysis showed no more starting material, the mixture was acidified with 1M HCl. The EtOH was evaporated and the remaining residue filtered to yield 30 mg (70%) of the above diacid as a brown impure solid which was further purified through recrystallization in methanol and dichloromethane mixture to get colourless powder.

R_F ($MeOH/CH_2Cl_2$; 1.5:8.5)= 0.8

M. p. = >240 °C

^{1}H NMR (400.1 MHz, CD_3COOD): δ = 2.32 (br. s, 4 x 2 H, 3 / 5-H), 2.05 (br. s, 2 x 1 H, 4-H), 1.62-1.88 (m, 4 x 2 H, 2 / 6-H), 1.42 (t, ^3J = 4.1 Hz, 1 H, 1-H), 1.09-1.36 (m, 2 x 2 H, 1a, 6a-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 178.66 (s, C-7), 130.08 (s, C-2a / 5a), 41.51 (d, C-4), 41.41 (t, C-3 / 5), 24.18 (t, C-2 / 6), 24.76 (d, C-1), 20.58 (d, C-1a / 6a).

UV/Vis (CH_3CN): λ_{max} (lg ε) = 264 nm (3.83), 276 (3.84).

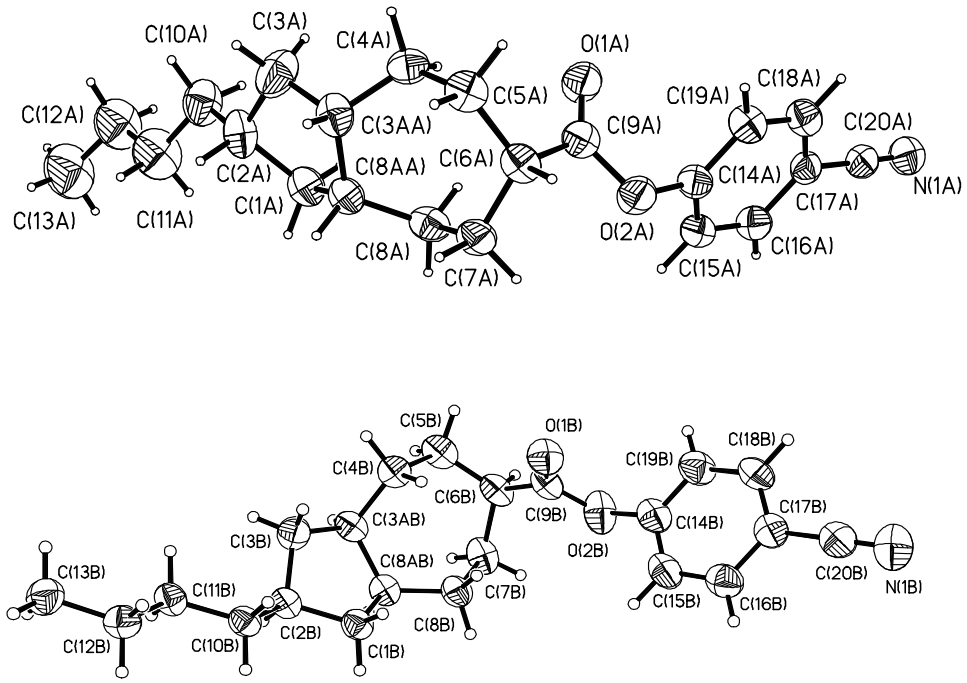
IR (KBr): $\tilde{\nu}$ = 3432 cm^{-1} (w), 3025 (w), 2911, 2895, 2830 (w), 2723, 2678, 2674, 2622, 2587 (w), 1687 (s, C=O), 1655, 1456, 1448, 1343, 1299, 1217, 1203, 1016 (w).

MS (EI, 70 eV): *m/z* (%) = 354 [M^+] (25), 336 [M^+-H_2O] (17), 308 [336-CO] (10), 177 [M^+ / 2]] (80), 159 [177-H_2O] (39), 131 [159–CO] (100), 91 [131–C_3H_4] (59).

HRMS $C_{22}H_{26}O_4$ Calcd. 354.18311; found 354.18257 ± 5 ppm

5. Single crystal X-ray structure data

5.1. 2-Butyl-decahydro-azulene-6-carboxylic acid 4-cyano-phenyl ester (85)



Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5395.1(14) pm	α= 92.349(6)°
	b = 10261(3) pm	β= 91.165(6)°
	c = 35578(9) pm	γ = 90.576(6)°
Volume, Z	1.9674(9) nm^3, 4	

Bond lengths [A]

O(1A)-C(9A)	1.191(4)	O(2A)-C(9A)	1.367(4)
O(2A)-C(14A)	1.397(4)	N(1A)-C(20A)	1.146(4)
C(1A)-C(8AA)	1.517(4)	C(1A)-C(2A)	1.521(4)
C(1A)-H(1AA)	0.9900	C(1A)-H(1AB)	0.9900
C(2A)-C(3A)	1.502(4)	C(2A)-C(10A)	1.536(4)
C(2A)-H(2AA)	1.0000	C(3A)-C(3AA)	1.540(4)
C(3A)-H(3AB)	0.9900	C(3A)-H(3AC)	0.9900
C(3AA)-C(4A)	1.508(4)	C(3AA)-C(8AA)	1.575(4)
C(3AA)-H(3AA)	1.0000	C(4A)-C(5A)	1.506(4)
C(4A)-H(4AA)	0.9900	C(4A)-H(4AB)	0.9900
C(5A)-C(6A)	1.536(4)	C(5A)-H(5AA)	0.9900
C(5A)-H(5AB)	0.9900	C(6A)-C(9A)	1.497(4)
C(6A)-C(7A)	1.533(4)	C(6A)-H(6AA)	1.0000
C(7A)-C(8A)	1.534(4)	C(7A)-H(7AA)	0.9900

C(7A)-H(7AB)	0.9900	C(8A)-C(8AA)	1.528(4)
C(8A)-H(8AB)	0.9900	C(8A)-H(8AC)	0.9900
C(8AA)-H(8AA)	1.0000	C(10A)-C(11A)	1.468(4)
C(10A)-H(10A)	0.9900	C(10A)-H(10B)	0.9900
C(11A)-C(12A)	1.462(4)	C(11A)-H(11A)	0.9900
C(11A)-H(11B)	0.9900	C(12A)-C(13A)	1.451(4)
C(12A)-H(12A)	0.9900	C(12A)-H(12D)	0.9900
C(13A)-H(13A)	0.9800	C(13A)-H(13B)	0.9800
C(13A)-H(13E)	0.9800	C(14A)-C(15A)	1.358(4)
C(14A)-C(19A)	1.370(4)	C(15A)-C(16A)	1.392(4)
C(15A)-H(15A)	0.9500	C(16A)-C(17A)	1.390(4)
C(16A)-H(16A)	0.9500	C(17A)-C(18A)	1.377(4)
C(17A)-C(20A)	1.446(5)	C(18A)-C(19A)	1.378(4)
C(18A)-H(18A)	0.9500	C(19A)-H(19A)	0.9500
O(1B)-C(9B)	1.188(4)	O(2B)-C(9B)	1.353(4)
O(2B)-C(14B)	1.405(5)	N(1B)-C(20B)	1.142(5)
C(1B)-C(2B)	1.511(3)	C(1B)-C(8AB)	1.516(4)
C(1B)-H(1BA)	0.9900	C(1B)-H(1BB)	0.9900
C(2B)-C(3B)	1.519(4)	C(2B)-C(10B)	1.523(4)
C(2B)-H(2BA)	1.0000	C(3B)-C(3AB)	1.556(4)
C(3B)-H(3BA)	0.9900	C(3B)-H(3BB)	0.9900
C(3AB)-C(4B)	1.529(4)	C(3AB)-C(8AB)	1.565(4)
C(3AB)-H(3AD)	1.0000	C(4B)-C(5B)	1.549(4)
C(4B)-H(4BA)	0.9900	C(4B)-H(4BB)	0.9900
C(5B)-C(6B)	1.514(4)	C(5B)-H(5BA)	0.9900
C(5B)-H(5BB)	0.9900	C(6B)-C(9B)	1.480(5)
C(6B)-C(7B)	1.541(4)	C(6B)-H(6BA)	1.0000
C(7B)-C(8B)	1.541(4)	C(7B)-H(7BA)	0.9900
C(7B)-H(7BB)	0.9900	C(8B)-C(8AB)	1.507(3)
C(8B)-H(8BA)	0.9900	C(8B)-H(8BB)	0.9900
C(8AB)-H(8AD)	1.0000	C(10B)-C(11B)	1.506(3)
C(10B)-H(10C)	0.9900	C(10B)-H(10D)	0.9900
C(11B)-C(12B)	1.509(4)	C(11B)-H(11C)	0.9900
C(11B)-H(11D)	0.9900	C(12B)-C(13B)	1.522(3)
C(12B)-H(12B)	0.9900	C(12B)-H(12C)	0.9900
C(13B)-H(13C)	0.9800	C(13B)-H(13D)	0.9800
C(13B)-H(13F)	0.9800	C(14B)-C(15B)	1.351(5)
C(14B)-C(19B)	1.356(5)	C(15B)-C(16B)	1.402(5)
C(15B)-H(15B)	0.9500	C(16B)-C(17B)	1.390(5)
C(16B)-H(16B)	0.9500	C(17B)-C(18B)	1.386(5)
C(17B)-C(20B)	1.459(5)	C(18B)-C(19B)	1.372(5)
C(18B)-H(18B)	0.9500	C(19B)-H(19B)	0.9500

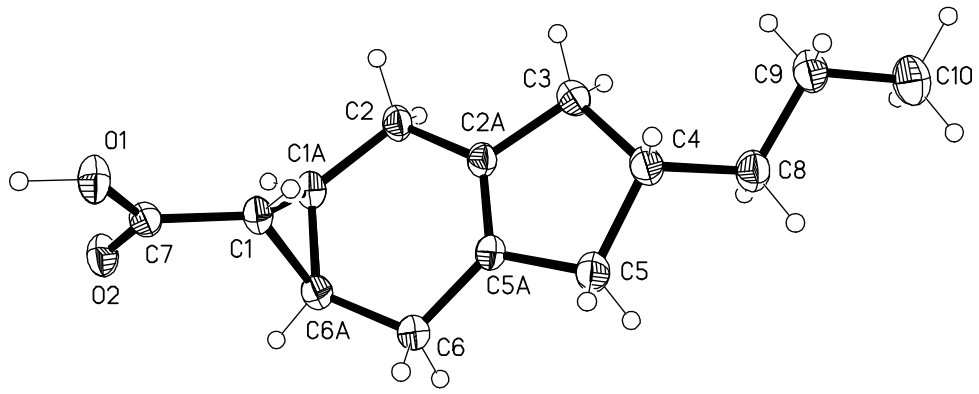
Bond angles [°]

C(9A)-O(2A)-C(14A)	119.2(3)	C(8AA)-C(1A)-C(2A)	104.9(3)
C(8AA)-C(1A)-H(1AA)	110.8	C(2A)-C(1A)-H(1AA)	110.8
C(8AA)-C(1A)-H(1AB)	110.8	C(2A)-C(1A)-H(1AB)	110.8
H(1AA)-C(1A)-H(1AB)	108.9	C(3A)-C(2A)-C(1A)	101.3(3)
C(3A)-C(2A)-C(10A)	113.2(3)	C(1A)-C(2A)-C(10A)	117.2(3)
C(3A)-C(2A)-H(2AA)	108.2	C(1A)-C(2A)-H(2AA)	108.2

C(10A)-C(2A)-H(2AA)	108.2	C(2A)-C(3A)-C(3AA)	106.8(3)
C(2A)-C(3A)-H(3AB)	110.4	C(3AA)-C(3A)-H(3AB)	110.4
C(2A)-C(3A)-H(3AC)	110.4	C(3AA)-C(3A)-H(3AC)	110.4
H(3AB)-C(3A)-H(3AC)	108.6	C(4A)-C(3AA)-C(3A)	111.6(3)
C(4A)-C(3AA)-C(8AA)	117.4(3)	C(3A)-C(3AA)-C(8AA)	104.3(3)
C(4A)-C(3AA)-H(3AA)	107.7	C(3A)-C(3AA)-H(3AA)	107.7
C(8AA)-C(3AA)-H(3AA)	107.7	C(5A)-C(4A)-C(3AA)	117.1(3)
C(5A)-C(4A)-H(4AA)	108.0	C(3AA)-C(4A)-H(4AA)	108.0
C(5A)-C(4A)-H(4AB)	108.0	C(3AA)-C(4A)-H(4AB)	108.0
H(4AA)-C(4A)-H(4AB)	107.3	C(4A)-C(5A)-C(6A)	117.5(3)
C(4A)-C(5A)-H(5AA)	107.9	C(6A)-C(5A)-H(5AA)	107.9
C(4A)-C(5A)-H(5AB)	107.9	C(6A)-C(5A)-H(5AB)	107.9
H(5AA)-C(5A)-H(5AB)	107.2	C(9A)-C(6A)-C(7A)	110.2(3)
C(9A)-C(6A)-C(5A)	110.3(3)	C(7A)-C(6A)-C(5A)	115.5(3)
C(9A)-C(6A)-H(6AA)	106.8	C(7A)-C(6A)-H(6AA)	106.8
C(5A)-C(6A)-H(6AA)	106.8	C(6A)-C(7A)-C(8A)	114.8(3)
C(6A)-C(7A)-H(7AA)	108.6	C(8A)-C(7A)-H(7AA)	108.6
C(6A)-C(7A)-H(7AB)	108.6	C(8A)-C(7A)-H(7AB)	108.6
H(7AA)-C(7A)-H(7AB)	107.6	C(8AA)-C(8A)-C(7A)	115.5(3)
C(8AA)-C(8A)-H(8AB)	108.4	C(7A)-C(8A)-H(8AB)	108.4
C(8AA)-C(8A)-H(8AC)	108.4	C(7A)-C(8A)-H(8AC)	108.4
H(8AB)-C(8A)-H(8AC)	107.5	C(1A)-C(8AA)-C(8A)	114.2(3)
C(1A)-C(8AA)-C(3AA)	104.1(3)	C(8A)-C(8AA)-C(3AA)	116.0(3)
C(1A)-C(8AA)-H(8AA)	107.3	C(8A)-C(8AA)-H(8AA)	107.3
C(3AA)-C(8AA)-H(8AA)	107.3	O(1A)-C(9A)-O(2A)	121.1(4)
O(1A)-C(9A)-C(6A)	127.8(4)	O(2A)-C(9A)-C(6A)	111.1(4)
C(11A)-C(10A)-C(2A)	114.8(3)	C(11A)-C(10A)-H(10A)	108.6
C(2A)-C(10A)-H(10A)	108.6	C(11A)-C(10A)-H(10B)	108.6
C(2A)-C(10A)-H(10B)	108.6	H(10A)-C(10A)-H(10B)	107.6
C(12A)-C(11A)-C(10A)	115.6(4)	C(12A)-C(11A)-H(11A)	108.4
C(10A)-C(11A)-H(11A)	108.4	C(12A)-C(11A)-H(11B)	108.4
C(10A)-C(11A)-H(11B)	108.4	H(11A)-C(11A)-H(11B)	107.4
C(13A)-C(12A)-C(11A)	114.9(4)	C(13A)-C(12A)-H(12A)	108.5
C(11A)-C(12A)-H(12A)	108.5	C(13A)-C(12A)-H(12D)	108.5
C(11A)-C(12A)-H(12D)	108.5	H(12A)-C(12A)-H(12D)	107.5
C(12A)-C(13A)-H(13A)	109.5	C(12A)-C(13A)-H(13B)	109.5
H(13A)-C(13A)-H(13B)	109.5	C(12A)-C(13A)-H(13E)	109.5
H(13A)-C(13A)-H(13E)	109.5	H(13B)-C(13A)-H(13E)	109.5
C(15A)-C(14A)-C(19A)	122.3(4)	C(15A)-C(14A)-O(2A)	115.7(4)
C(19A)-C(14A)-O(2A)	121.9(4)	C(14A)-C(15A)-C(16A)	118.8(4)
C(14A)-C(15A)-H(15A)	120.6	C(16A)-C(15A)-H(15A)	120.6
C(17A)-C(16A)-C(15A)	119.3(4)	C(17A)-C(16A)-H(16A)	120.4
C(15A)-C(16A)-H(16A)	120.4	C(18A)-C(17A)-C(16A)	120.8(4)
C(18A)-C(17A)-C(20A)	119.4(4)	C(16A)-C(17A)-C(20A)	119.8(4)
C(17A)-C(18A)-C(19A)	119.2(4)	C(17A)-C(18A)-H(18A)	120.4
C(19A)-C(18A)-H(18A)	120.4	C(14A)-C(19A)-C(18A)	119.6(4)
C(14A)-C(19A)-H(19A)	120.2	C(18A)-C(19A)-H(19A)	120.2
N(1A)-C(20A)-C(17A)	177.4(5)	C(9B)-O(2B)-C(14B)	118.5(3)
C(2B)-C(1B)-C(8AB)	105.4(3)	C(2B)-C(1B)-H(1BA)	110.7
C(8AB)-C(1B)-H(1BA)	110.7	C(2B)-C(1B)-H(1BB)	110.7
C(8AB)-C(1B)-H(1BB)	110.7	H(1BA)-C(1B)-H(1BB)	108.8

C(1B)-C(2B)-C(3B)	101.2(3)	C(1B)-C(2B)-C(10B)	116.9(3)
C(3B)-C(2B)-C(10B)	114.9(3)	C(1B)-C(2B)-H(2BA)	107.8
C(3B)-C(2B)-H(2BA)	107.8	C(10B)-C(2B)-H(2BA)	107.8
C(2B)-C(3B)-C(3AB)	107.2(3)	C(2B)-C(3B)-H(3BA)	110.3
C(3AB)-C(3B)-H(3BA)	110.3	C(2B)-C(3B)-H(3BB)	110.3
C(3AB)-C(3B)-H(3BB)	110.3	H(3BA)-C(3B)-H(3BB)	108.5
C(4B)-C(3AB)-C(3B)	111.2(3)	C(4B)-C(3AB)-C(8AB)	115.7(3)
C(3B)-C(3AB)-C(8AB)	104.0(3)	C(4B)-C(3AB)-H(3AD)	108.5
C(3B)-C(3AB)-H(3AD)	108.5	C(8AB)-C(3AB)-H(3AD)	108.5
C(3AB)-C(4B)-C(5B)	116.9(3)	C(3AB)-C(4B)-H(4BA)	108.1
C(5B)-C(4B)-H(4BA)	108.1	C(3AB)-C(4B)-H(4BB)	108.1
C(5B)-C(4B)-H(4BB)	108.1	H(4BA)-C(4B)-H(4BB)	107.3
C(6B)-C(5B)-C(4B)	116.6(3)	C(6B)-C(5B)-H(5BA)	108.1
C(4B)-C(5B)-H(5BA)	108.1	C(6B)-C(5B)-H(5BB)	108.1
C(4B)-C(5B)-H(5BB)	108.1	H(5BA)-C(5B)-H(5BB)	107.3
C(9B)-C(6B)-C(5B)	112.0(4)	C(9B)-C(6B)-C(7B)	109.9(3)
C(5B)-C(6B)-C(7B)	114.5(3)	C(9B)-C(6B)-H(6BA)	106.6
C(5B)-C(6B)-H(6BA)	106.6	C(7B)-C(6B)-H(6BA)	106.6
C(8B)-C(7B)-C(6B)	114.6(3)	C(8B)-C(7B)-H(7BA)	108.6
C(6B)-C(7B)-H(7BA)	108.6	C(8B)-C(7B)-H(7BB)	108.6
C(6B)-C(7B)-H(7BB)	108.6	H(7BA)-C(7B)-H(7BB)	107.6
C(8AB)-C(8B)-C(7B)	115.6(3)	C(8AB)-C(8B)-H(8BA)	108.4
C(7B)-C(8B)-H(8BA)	108.4	C(8AB)-C(8B)-H(8BB)	108.4
C(7B)-C(8B)-H(8BB)	108.4	H(8BA)-C(8B)-H(8BB)	107.4
C(8B)-C(8AB)-C(1B)	114.4(3)	C(8B)-C(8AB)-C(3AB)	117.7(3)
C(1B)-C(8AB)-C(3AB)	104.2(3)	C(8B)-C(8AB)-H(8AD)	106.6
C(1B)-C(8AB)-H(8AD)	106.6	C(3AB)-C(8AB)-H(8AD)	106.6
O(1B)-C(9B)-O(2B)	120.6(4)	O(1B)-C(9B)-C(6B)	128.8(5)
O(2B)-C(9B)-C(6B)	110.6(4)	C(11B)-C(10B)-C(2B)	114.8(3)
C(11B)-C(10B)-H(10C)	108.6	C(2B)-C(10B)-H(10C)	108.6
C(11B)-C(10B)-H(10D)	108.6	C(2B)-C(10B)-H(10D)	108.6
H(10C)-C(10B)-H(10D)	107.5	C(10B)-C(11B)-C(12B)	115.5(3)
C(10B)-C(11B)-H(11C)	108.4	C(12B)-C(11B)-H(11C)	108.4
C(10B)-C(11B)-H(11D)	108.4	C(12B)-C(11B)-H(11D)	108.4
H(11C)-C(11B)-H(11D)	107.5	C(11B)-C(12B)-C(13B)	113.6(3)
C(11B)-C(12B)-H(12B)	108.8	C(13B)-C(12B)-H(12B)	108.8
C(11B)-C(12B)-H(12C)	108.8	C(13B)-C(12B)-H(12C)	108.8
H(12B)-C(12B)-H(12C)	107.7	C(12B)-C(13B)-H(13C)	109.5
C(12B)-C(13B)-H(13D)	109.5	H(13C)-C(13B)-H(13D)	109.5
C(12B)-C(13B)-H(13F)	109.5	H(13C)-C(13B)-H(13F)	109.5
H(13D)-C(13B)-H(13F)	109.5	C(15B)-C(14B)-C(19B)	121.9(5)
C(15B)-C(14B)-O(2B)	116.7(5)	C(19B)-C(14B)-O(2B)	121.2(6)
C(14B)-C(15B)-C(16B)	119.8(5)	C(14B)-C(15B)-H(15B)	120.1
C(16B)-C(15B)-H(15B)	120.1	C(17B)-C(16B)-C(15B)	118.2(5)
C(17B)-C(16B)-H(16B)	120.9	C(15B)-C(16B)-H(16B)	120.9
C(18B)-C(17B)-C(16B)	120.6(5)	C(18B)-C(17B)-C(20B)	120.3(5)
C(16B)-C(17B)-C(20B)	119.1(5)	C(19B)-C(18B)-C(17B)	119.4(4)
C(19B)-C(18B)-H(18B)	120.3	C(17B)-C(18B)-H(18B)	120.3
C(14B)-C(19B)-C(18B)	120.0(5)	C(14B)-C(19B)-H(19B)	120.0
C(18B)-C(19B)-H(19B)	120.0	N(1B)-C(20B)-C(17B)	178.4(6

5.2. 4-Propyl-1, 1a, 2, 3, 4, 5, 6, 6a-octahydrocyclopropa[*f*] indene-1-carboxylic acid (67)



Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8072.8(12) pm	α= 90°
	b = 7190.0(11) pm	β= 93.379(8)°
	c = 2087.2(3) pm	γ = 90°
Volume, Z	1.2094(3) nm^3, 4	

Bond lengths [A]

O(1)-C(7)	1.2996(16)	O(2)-C(7)	1.2482(16)
C(1)-C(7)	1.4685(18)	C(1)-C(6A)	1.5214(18)
C(1)-C(1A)	1.5255(18)	C(1A)-C(6A)	1.4943(19)
C(1A)-C(2)	1.5150(17)	C(2)-C(2A)	1.4975(17)
C(2A)-C(5A)	1.3294(18)	C(2A)-C(3)	1.5044(18)
C(3)-C(4)	1.5577(19)	C(4)-C(8)	1.5211(18)
C(4)-C(5)	1.5481(19)	C(5)-C(5A)	1.5034(18)
C(5A)-C(6)	1.4963(18)	C(6)-C(6A)	1.5134(18)
C(8)-C(9)	1.5143(19)	C(9)-C(10)	1.5192(19)

Bond angles [°].

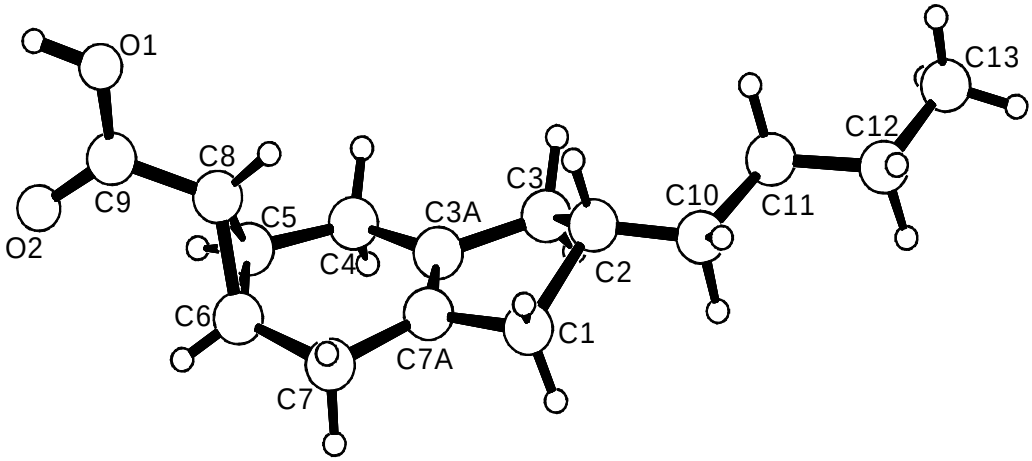
C(7)-C(1)-C(6A)	119.38(12)	C(7)-C(1)-C(1A)	118.35(11)
C(6A)-C(1)-C(1A)	58.74(8)	C(6A)-C(1A)-C(2)	121.06(11)
C(6A)-C(1A)-C(1)	60.49(9)	C(2)-C(1A)-C(1)	117.53(11)
C(2A)-C(2)-C(1A)	112.89(11)	C(5A)-C(2A)-C(2)	124.95(12)
C(5A)-C(2A)-C(3)	112.37(12)	C(2)-C(2A)-C(3)	122.62(11)
C(2A)-C(3)-C(4)	104.51(10)	C(8)-C(4)-C(5)	112.86(12)
C(8)-C(4)-C(3)	113.62(12)	C(5)-C(4)-C(3)	105.30(11)

C(5A)-C(5)-C(4)	104.92(11)	C(2A)-C(5A)-C(6)	125.16(12)
C(2A)-C(5A)-C(5)	112.15(12)	C(6)-C(5A)-C(5)	122.61(12)
C(5A)-C(6)-C(6A)	112.98(11)	C(1A)-C(6A)-C(6)	120.71(11)
C(1A)-C(6A)-C(1)	60.77(9)	C(6)-C(6A)-C(1)	117.99(12)
O(2)-C(7)-O(1)	123.42(12)	O(2)-C(7)-C(1)	121.60(12)
O(1)-C(7)-C(1)	114.98(12)	C(9)-C(8)-C(4)	114.45(12)
C(8)-C(9)-C(10)	113.18(13)		

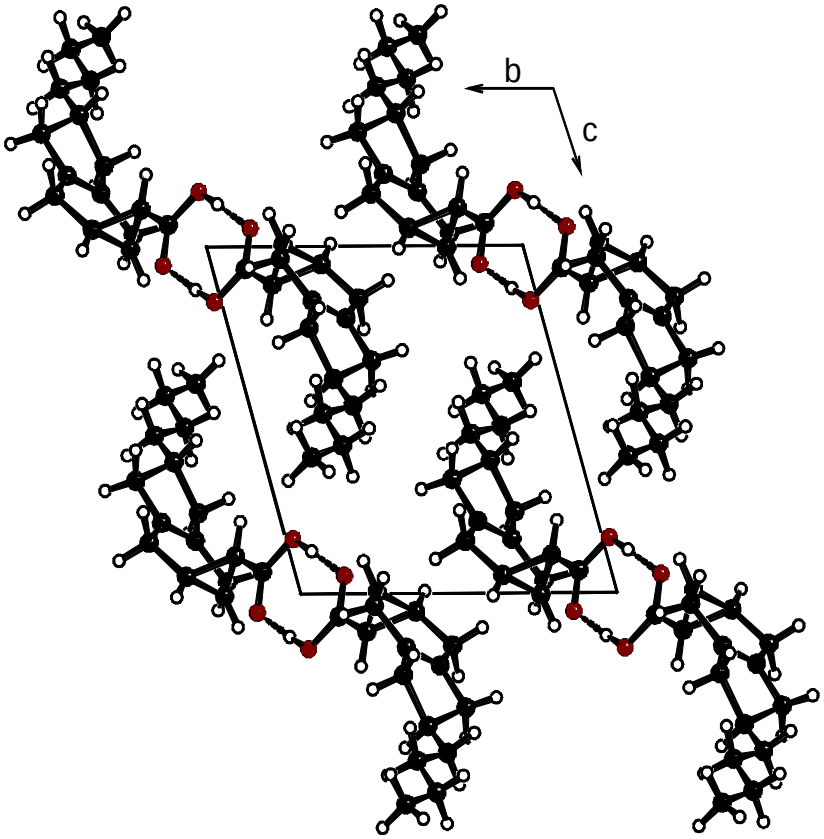
Torsion angles [°].

C(7)-C(1)-C(1A)-C(6A)	-108.93(13)	C(7)-C(1)-C(1A)-C(2)	139.13(12)
C(6A)-C(1)-C(1A)-C(2)	-111.94(13)	C(6A)-C(1A)-C(2)-C(2A)	-10.92(17)
C(1)-C(1A)-C(2)-C(2A)	59.54(15)	C(1A)-C(2)-C(2A)-C(5A)	11.79(18)
C(1A)-C(2)-C(2A)-C(3)	-171.12(12)	C(5A)-C(2A)-C(3)-C(4)	-5.10(15)
C(2)-C(2A)-C(3)-C(4)	177.48(12)	C(2A)-C(3)-C(4)-C(8)	132.12(12)
C(2A)-C(3)-C(4)-C(5)	8.13(15)	C(8)-C(4)-C(5)-C(5A)	-132.80(13)
C(3)-C(4)-C(5)-C(5A)	-8.32(15)	C(2)-C(2A)-C(5A)-C(6)	0.2(2)
C(3)-C(2A)-C(5A)-C(6)	-177.17(12)	C(2)-C(2A)-C(5A)-C(5)	177.02(12)
C(3)-C(2A)-C(5A)-C(5)	-0.33(16)	C(4)-C(5)-C(5A)-C(2A)	5.66(16)
C(4)-C(5)-C(5A)-C(6)	-177.41(12)	C(2A)-C(5A)-C(6)-C(6A)	-12.5(2)
C(5)-C(5A)-C(6)-C(6A)	171.02(12)	C(2)-C(1A)-C(6A)-C(6)	-0.84(19)
C(1)-C(1A)-C(6A)-C(6)	-107.04(14)	C(2)-C(1A)-C(6A)-C(1)	106.21(13)
C(5A)-C(6)-C(6A)-C(1A)	12.19(19)	C(5A)-C(6)-C(6A)-C(1)	-58.69(16)
C(7)-C(1)-C(6A)-C(1A)	107.21(13)	C(7)-C(1)-C(6A)-C(6)	-141.37(12)
C(1A)-C(1)-C(6A)-C(6)	111.42(13)	C(6A)-C(1)-C(7)-O(2)	-28.30(19)
C(1A)-C(1)-C(7)-O(2)	39.80(19)	C(6A)-C(1)-C(7)-O(1)	152.42(12)
C(1A)-C(1)-C(7)-O(1)	-139.48(12)	C(5)-C(4)-C(8)-C(9)	-175.58(12)
C(3)-C(4)-C(8)-C(9)	64.63(17)	C(4)-C(8)-C(9)-C(10)	-179.71(12)

5.3. 2-Butyl-1, 2, 3, 4, 5, 6, 7, 8-octahydrocyclopropa[*f*] indene-8-carboxylic acid (68)



Molecular structure of **68**. It is shown only one of the disordered positions of C2, C11, C12 and C13.



Packing arrangement of **68**. View along the crystallographic a-axis. Hydrogen bonds are shown as fragmented lines.

Crystal system	Triclinic	
Space group	P(-1)	
Unit cell dimensions	a = 8225.5(7) pm	α= 103.664(2)°
	b = 9463.6(8) pm	β= 94.352(2)°
	c = 9649.8(8) pm	γ = 107.582(2)°
Volume, Z	0.6870(1) nm^3, 2	

Bond lengths [A]

O1-C9	1.303(3)	O1-H1	0.93(3)
O2-C9	1.229(2)	C1-C2A	1.485(6)
C1-C7A	1.499(3)	C1-C2	1.626(6)
C1-H1A	0.97(3)	C1-H1B	0.97(3)
C2-C10	1.417(6)	C2-C3	1.558(6)
C2-H2	0.9800	C2A-C10	1.438(6)
C2A-C3	1.584(6)	C2A-H2A	0.9800
C2A-H10A	1.4744	C3-C3A	1.496(3)
C3-H3A	0.90(3)	C3-H3B	0.98(3)
C3A-C7A	1.314(3)	C3A-C4	1.494(3)
C4-C5	1.499(3)	C4-H4A	0.98(3)
C4-H4B	0.96(3)	C5-C6	1.477(3)
C5-C8	1.513(3)	C5-H5	0.93(2)
C6-C7	1.509(3)	C6-C8	1.512(3)
C6-H6	0.89(2)	C7-C7A	1.496(3)
C7-H7A	0.98(3)	C7-H7B	1.02(3)
C8-C9	1.467(3)	C8-H8	0.986(18)
C10-C11B	1.380(16)	C10-C11A	1.500(17)
C10-C11	1.544(8)	C10-H10A	0.9972
C10-H10B	0.9546	C11-C12	1.493(12)
C11-H11A	0.9700	C11-H11B	0.9700
C12-C13	1.426(18)	C12-H12A	0.9700
C12-H12B	0.9700	C13-H13A	0.9600
C13-H13B	0.9600	C13-H13C	0.9600
C11A-C12A	1.39(5)	C11A-H11C	0.9700
C11A-H11D	0.9700	C12A-C13A	1.29(5)
C12A-H12C	0.9700	C12A-H12D	0.9700
C13A-H13D	0.9600	C13A-H13E	0.9600
C13A-H13F	0.9600	C11B-C12B	1.55(2)
C11B-H11E	0.9700	C11B-H11F	0.9700
C12B-C13B	1.85(3)	C12B-H12E	0.9700
C12B-H12F	0.9700	C13B-H13G	0.9600
C13B-H13H	0.9600	C13B-H13I	0.9600

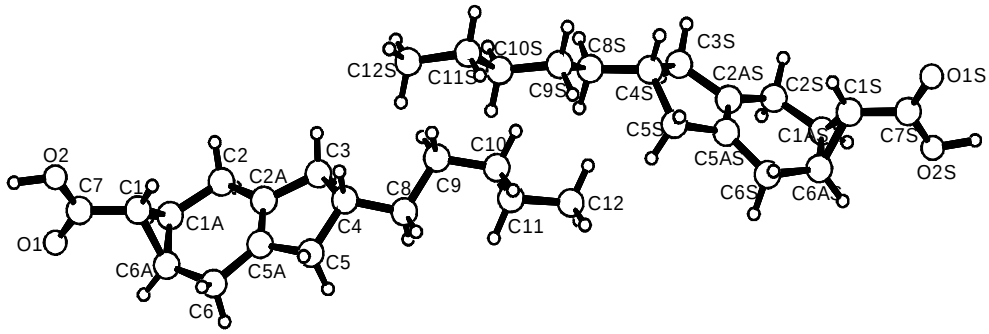
Bond angles [°]

C9-O1-H1	112.3(15)	C2A-C1-C7A	105.4(3)
C2A-C1-C2	31.3(2)	C7A-C1-C2	101.3(2)
C2A-C1-H1A	121.6(17)	C7A-C1-H1A	112.1(16)
C2-C1-H1A	96.9(17)	C2A-C1-H1B	89(2)
C7A-C1-H1B	112(2)	C2-C1-H1B	118(2)
H1A-C1-H1B	115(3)	C10-C2-C3	118.1(4)

C10-C2-C1	114.4(4)	C3-C2-C1	99.5(3)
C10-C2-H2	108.1	C3-C2-H2	108.1
C1-C2-H2	108.1	C10-C2A-C1	122.3(4)
C10-C2A-C3	115.1(4)	C1-C2A-C3	104.7(4)
C10-C2A-H2A	104.3	C1-C2A-H2A	104.3
C3-C2A-H2A	104.3	C10-C2A-H10A	40.0
C1-C2A-H10A	124.1	C3-C2A-H10A	131.2
H2A-C2A-H10A	65.0	C3A-C3-C2	103.5(2)
C3A-C3-C2A	103.2(3)	C2-C3-C2A	31.4(2)
C3A-C3-H3A	109.6(19)	C2-C3-H3A	121(2)
C2A-C3-H3A	93(2)	C3A-C3-H3B	116(2)
C2-C3-H3B	96(2)	C2A-C3-H3B	122(2)
H3A-C3-H3B	110(3)	C7A-C3A-C4	125.4(2)
C7A-C3A-C3	111.6(2)	C4-C3A-C3	123.1(2)
C3A-C4-C5	113.1(2)	C3A-C4-H4A	105.0(16)
C5-C4-H4A	111.7(16)	C3A-C4-H4B	107.6(19)
C5-C4-H4B	113.7(19)	H4A-C4-H4B	105(3)
C6-C5-C4	120.4(2)	C6-C5-C8	60.74(15)
C4-C5-C8	118.1(2)	C6-C5-H5	120.1(14)
C4-C5-H5	113.7(14)	C8-C5-H5	113.2(14)
C5-C6-C7	121.5(2)	C5-C6-C8	60.79(14)
C7-C6-C8	118.8(2)	C5-C6-H6	115.1(16)
C7-C6-H6	115.2(16	C8-C6-H6	114.5(16)
C7A-C7-C6	112.5(2)	C7A-C7-H7A	108.3(17)
C6-C7-H7A	110.0(17)	C7A-C7-H7B	106.2(15)
C6-C7-H7B	112.5(15)	H7A-C7-H7B	107(2)
C3A-C7A-C7	124.4(2)	C3A-C7A-C1	112.3(2)
C7-C7A-C1	123.3(2)	C9-C8-C6	119.13(19)
C9-C8-C5	116.95(18)	C6-C8-C5	58.47(15)
C9-C8-H8	116.1(10)	C6-C8-H8	116.0(10)
C5-C8-H8	117.9(10)	O2-C9-O1	122.5(2)
O2-C9-C8	123.0(2)	O1-C9-C8	114.47(19)
C11B-C10-C2	128.1(7)	C11B-C10-C2A	121.6(7)
C2-C10-C2A	34.6(2)	C11B-C10-C11A	38.4(8)
C2-C10-C11A	111.9(7)	C2A-C10-C11A	131.8(7)
C11B-C10-C11	19.3(6)	C2-C10-C11	118.8(4)
C2A-C10-C11	126.0(4)	C11A-C10-C11	19.6(6)
C11B-C10-H10A	85.0	C2-C10-H10A	106.4
C2A-C10-H10A	71.9	C11A-C10-H10A	123.2
C11-C10-H10A	104.2	C11B-C10-H10B	114.0
C2-C10-H10B	110.9	C2A-C10-H10B	123.7
C11A-C10-H10B	97.4	C11-C10-H10B	109.4
H10A-C10-H10B	106.2	C12-C11-C10	118.2(6)
C12-C11-H11A	107.8	C10-C11-H11A	107.8
C12-C11-H11B	107.8	C10-C11-H11B	107.8
H11A-C11-H11B	107.1	C13-C12-C11	117.0(9)
C13-C12-H12A	108.0	C11-C12-H12A	108.0
C13-C12-H12B	108.0	C11-C12-H12B	108.0
H12A-C12-H12B	107.3	C12A-C11A-C10	108(2)
C12A-C11A-H11C	110.2	C10-C11A-H11C	110.2
C12A-C11A-H11D	110.2	C10-C11A-H11D	110.2

H11C-C11A-H11D	108.5	C13A-C12A-C11A	125(4)
C13A-C12A-H12C	106.0	C11A-C12A-H12C	106.0
C13A-C12A-H12D	106.0	C11A-C12A-H12D	106.0
H12C-C12A-H12D	106.3	C12A-C13A-H13D	109.5
C12A-C13A-H13E	109.5	H13D-C13A-H13E	109.5
C12A-C13A-H13F	109.5	H13D-C13A-H13F	109.5
H13E-C13A-H13F	109.5	C10-C11B-C12B	113.2(12)
C10-C11B-H11E	108.9	C12B-C11B-H11E	108.9
C10-C11B-H11F	108.9	C12B-C11B-H11F	108.9
H11E-C11B-H11F	107.8	C11B-C12B-C13B	104.5(13)
C11B-C12B-H12E	110.9	C13B-C12B-H12E	110.9
C11B-C12B-H12F	110.9	C13B-C12B-H12F	110.9
H12E-C12B-H12F	109		

5.4. 4-Pentyl-1, 1a, 2, 3, 4, 5, 6, 6a-octahydrocyclopropa[*f*] indene-1-carboxylic acid (69)



Molecular structure of **69**. It is shown only one of the disordered positions of the upper of both molecules.

Crystal system	Triclinic	
Space group	P(-1)	
Unit cell dimensions	a = 8794.7(7) pm	α= 86.694(2)°
	b = 8931.1(7) pm	β= 89.283(2)°
	c = 1835.9(1) pm	γ = 79.071(2)°
Volume, Z	1.4135(2) nm^3, 2	

Bond lengths [A]

O1-C7	1.2580(18)	O2-C7	1.2874(18)
O2-H1O	1.04(3)	O1S-C7S	1.2533(18)
O2S-C7S	1.2885(18)	O2S-H1OS	1.08(3)
C1-C7	1.465(2)	C1-C6A	1.5254(19)
C1-C1A	1.5308(19)	C1-H1	0.953(17)
C1A-C6A	1.4943(19)	C1A-C2	1.516(2)
C1A-H1A	0.963(18)	C2-C2A	1.496(2)
C2-H2A	0.990(18)	C2-H2B	0.950(18)
C2A-C5A	1.332(2)	C2A-C3	1.504(2)
C3-C4	1.554(2)	C3-H3A	0.952(18)
C3-H3B	1.000(19)	C4-C8	1.520(2)
C4-C5	1.547(2)	C4-H4	1.037(18)
C5-C5A	1.501(2)	C5-H5A	0.998(18)
C5-H5B	0.983(19)	C5A-C6	1.492(2)
C6-C6A	1.510(2)	C6-H6A	0.968(18)
C6-H6B	0.974(19)	C6A-H6	0.937(17)
C8-C9	1.517(2)	C8-H8A	1.026(19)
C8-H8B	1.049(19)	C9-C10	1.530(2)
C9-H9A	0.98(2)	C9-H9B	0.98(2)
C10-C11	1.518(2)	C10-H10A	0.98(2)
C10-H10B	1.02(2)	C11-C12	1.512(2)
C11-H11A	1.03(2)	C11-H11B	1.06(2)
C12-H12A	0.97(2)	C12-H12B	0.99(3)

C12-H12C	1.01(3)	C1S-C7S	1.466(2)
C1S-C1AS	1.523(2)	C1S-C6AS	1.525(2)
C1S-H1S	0.955(17)	C1AS-C6AS	1.492(2)
C1AS-C2S	1.508(2)	C1AS-H1AS	0.960(19)
C2S-C2AS	1.490(2)	C2S-H2C	0.96(2)
C2S-H2D	0.99(2)	C2AS-C5AS	1.328(2)
C2AS-C3S	1.501(2)	C3S-C4T	1.553(9)
C3S-C4S	1.557(2)	C3S-H3C	0.93(2)
C3S-H3D	0.98(2)	C4S-C8S	1.502(2)
C4S-C5S	1.548(3)	C4S-H4AS	1.00(2)
C4T-C8S	1.439(9)	C4T-C5S	1.625(9)
C4T-H4T	1.0000	C4T-H8D	1.46(2)
C5S-C5AS	1.508(2)	C5S-H5C	0.96(2)
C5S-H5D	0.98(2)	C5AS-C6S	1.489(2)
C6S-C6AS	1.515(2)	C6S-H6C	0.95(2)
C6S-H6D	1.00(2)	C6AS-H6S	0.960(18)
C8S-C9T	1.407(13)	C8S-C9S	1.512(3)
C8S-H8C	1.00(2)	C8S-H8D	1.05(2)
C9S-C10S	1.513(3)	C9S-H9C	0.9900
C9S-H9D	0.9900	C10S-C11S	1.514(3)
C10S-H10C	0.9900	C10S-H10D	0.9900
C11S-C12S	1.518(3)	C11S-H11C	0.9900
C11S-H11D	0.9900	C12S-H12D	0.9800
C12S-H12E	0.9800	C12S-H12F	0.9800
C9T-C10T	1.56(2)	C9T-H9E	0.9900
C9T-H9F	0.9900	C9T-H8D	1.54(3)
C10T-C11T	1.59(2)	C10T-H10E	0.9900
C10T-H10F	0.9900	C11T-C12T	1.46(3)
C11T-H11E	0.9900	C11T-H11F	0.9900
C12T-H12G	0.9800	C12T-H12H	0.9800
C12T-H12I	0.9800		

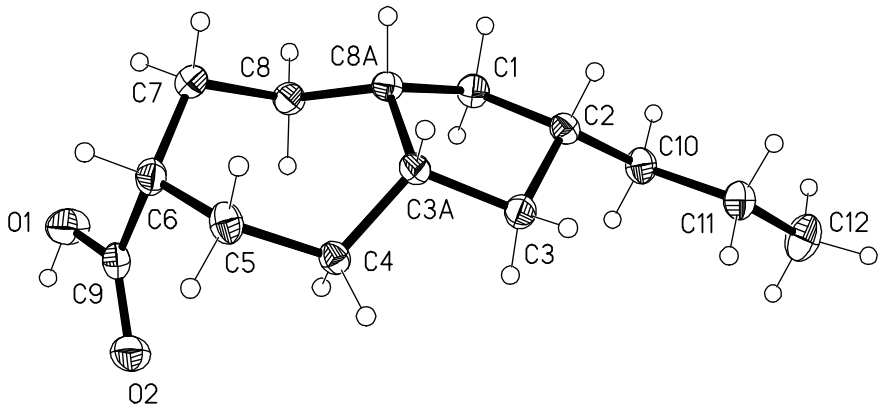
Bond angles [°]

C7-O2-H1O	111.5(16)	C7S-O2S-H1OS	113.1(16)
C7-C1-C6A	117.22(12)	C7-C1-C1A	119.78(12)
C6A-C1-C1A	58.54(9)	C7-C1-H1	113.8(10)
C6A-C1-H1	119.8(10)	C1A-C1-H1	117.0(10)
C6A-C1A-C2	120.51(13)	C6A-C1A-C1	60.55(9)
C2-C1A-C1	118.27(12)	C6A-C1A-H1A	116.2(10)
C2-C1A-H1A	116.4(10)	C1-C1A-H1A	113.0(10)
C2A-C2-C1A	113.36(12)	C2A-C2-H2A	108.7(10)
C1A-C2-H2A	107.7(10)	C2A-C2-H2B	110.0(10)
C1A-C2-H2B	110.6(10)	H2A-C2-H2B	106.2(14)
C5A-C2A-C2	125.61(13)	C5A-C2A-C3	111.34(13)
C2-C2A-C3	122.87(12)	C2A-C3-C4	104.41(12)
C2A-C3-H3A	112.3(11)	C4-C3-H3A	112.5(11)
C2A-C3-H3B	108.6(11)	C4-C3-H3B	112.1(11)
H3A-C3-H3B	106.9(15)	C8-C4-C5	114.36(12)
C8-C4-C3	114.29(13)	C5-C4-C3	104.27(12)
C8-C4-H4	108.8(10)	C5-C4-H4	107.0(10)

C3-C4-H4	107.7(10)	C5A-C5-C4	104.38(12)
C5A-C5-H5A	111.8(10)	C4-C5-H5A	110.8(10)
C5A-C5-H5B	110.0(11)	C4-C5-H5B	113.0(10)
H5A-C5-H5B	106.9(14)	C2A-C5A-C6	124.98(13)
C2A-C5A-C5	112.26(13)	C6-C5A-C5	122.57(12)
C5A-C6-C6A	113.26(12)	C5A-C6-H6A	110.4(10)
C6A-C6-H6A	108.7(10)	C5A-C6-H6B	109.1(11)
C6A-C6-H6B	109.2(11)	H6A-C6-H6B	105.9(15)
C1A-C6A-C6	121.77(13)	C1A-C6A-C1	60.91(9)
C6-C6A-C1	118.44(12)	C1A-C6A-H6	115.8(10)
C6-C6A-H6	115.1(10)	C1-C6A-H6	113.8(10)
O1-C7-O2	123.11(14)	O1-C7-C1	120.46(13)
O2-C7-C1	116.42(13)	C9-C8-C4	112.86(13)
C9-C8-H8A	109.7(10)	C4-C8-H8A	106.6(10)
C9-C8-H8B	110.7(10)	C4-C8-H8B	106.4(10)
H8A-C8-H8B	110.4(14)	C8-C9-C10	115.04(13)
C8-C9-H9A	108.9(12)	C10-C9-H9A	109.1(11)
C8-C9-H9B	108.8(11)	C10-C9-H9B	109.2(11)
H9A-C9-H9B	105.4(16)	C11-C10-C9	114.91(14)
C11-C10-H10A	105.9(12)	C9-C10-H10A	110.4(12)
C11-C10-H10B	107.6(10)	C9-C10-H10B	110.9(10)
H10A-C10-H10B	106.7(15)	C12-C11-C10	112.31(16)
C12-C11-H11A	110.8(11)	C10-C11-H11A	106.5(11)
C12-C11-H11B	109.6(12)	C10-C11-H11B	108.9(12)
H11A-C11-H11B	108.5(16)	C11-C12-H12A	111.9(12)
C11-C12-H12B	106.8(14)	H12A-C12-H12B	106.9(18)
C11-C12-H12C	111.0(15)	H12A-C12-H12C	107.4(19)
H12B-C12-H12C	113(2)	C7S-C1S-C1AS	118.26(13)
C7S-C1S-C6AS	120.27(13)	C1AS-C1S-C6AS	58.63(10)
C7S-C1S-H1S	115.1(10)	C1AS-C1S-H1S	116.7(10)
C6AS-C1S-H1S	116.3(10)	C6AS-C1AS-C2S	121.20(13)
C6AS-C1AS-C1S	60.77(10)	C2S-C1AS-C1S	118.54(14)
C6AS-C1AS-H1AS	115.7(11)	C2S-C1AS-H1AS	116.4(11)
C1S-C1AS-H1AS	112.2(11)	C2AS-C2S-C1AS	113.10(13)
C2AS-C2S-H2C	107.5(12)	C1AS-C2S-H2C	107.8(12)
C2AS-C2S-H2D	110.2(11)	C1AS-C2S-H2D	111.3(11)
H2C-C2S-H2D	106.5(16)	C5AS-C2AS-C2S	125.20(15)
C5AS-C2AS-C3S	111.99(14)	C2S-C2AS-C3S	122.76(14)
C2AS-C3S-C4T	102.5(3)	C2AS-C3S-C4S	103.93(13)
C4T-C3S-C4S	35.2(4)	C2AS-C3S-H3C	110.1(13)
C4T-C3S-H3C	84.4(13)	C4S-C3S-H3C	115.9(13)
C2AS-C3S-H3D	113.2(11)	C4T-C3S-H3D	135.6(12)
C4S-C3S-H3D	107.9(11)	H3C-C3S-H3D	106.1(17)
C8S-C4S-C5S	115.92(16)	C8S-C4S-C3S	113.41(15)
C5S-C4S-C3S	103.74(15)	C8S-C4S-H4AS	105.8(13)
C5S-C4S-H4AS	110.4(13)	C3S-C4S-H4AS	107.4(13)
C8S-C4T-C3S	117.4(6)	C8S-C4T-C5S	115.0(6)
C3S-C4T-C5S	100.4(5)	C8S-C4T-H4T	107.8
C3S-C4T-H4T	107.8	C5S-C4T-H4T	107.8
C8S-C4T-H8D	42.3(10)	C3S-C4T-H8D	139.1(11)
C5S-C4T-H8D	120.1(11)	H4T-C4T-H8D	66.5

C5AS-C5S-C4S	104.20(13)	C5AS-C5S-C4T	100.6(3)
C4S-C5S-C4T	34.4(3)	C5AS-C5S-H5C	112.6(13)
C4S-C5S-H5C	107.5(13)	C4T-C5S-H5C	136.4(13)
C5AS-C5S-H5D	111.9(13)	C4S-C5S-H5D	115.1(13)
C4T-C5S-H5D	86.0(13)	H5C-C5S-H5D	105.7(18)
C2AS-C5AS-C6S	124.89(15)	C2AS-C5AS-C5S	111.48(14)
C6S-C5AS-C5S	123.53(13)	C5AS-C6S-C6AS	113.34(13)
C5AS-C6S-H6C	108.6(12)	C6AS-C6S-H6C	111.0(12)
C5AS-C6S-H6D	110.2(12)	C6AS-C6S-H6D	108.3(12)
H6C-C6S-H6D	105.0(16)	C1AS-C6AS-C6S	120.34(14)
C1AS-C6AS-C1S	60.60(10)	C6S-C6AS-C1S	118.38(13)
C1AS-C6AS-H6S	116.4(11)	C6S-C6AS-H6S	116.5(10)
C1S-C6AS-H6S	112.5(11)	O1S-C7S-O2S	122.98(14)
O1S-C7S-C1S	119.58(13)	O2S-C7S-C1S	117.44(13)
C9T-C8S-C4T	125.4(6)	C9T-C8S-C4S	128.6(5)
C4T-C8S-C4S	37.2(4)	C9T-C8S-C9S	29.5(6)
C4T-C8S-C9S	135.3(4)	C4S-C8S-C9S	116.00(16)
C9T-C8S-H8C	118.3(12)	C4T-C8S-H8C	112.2(12)
C4S-C8S-H8C	110.0(11)	C9S-C8S-H8C	111.4(11)
C9T-C8S-H8D	76.3(14)	C4T-C8S-H8D	70.1(13)
C4S-C8S-H8D	106.2(13)	C9S-C8S-H8D	105.7(13)
H8C-C8S-H8D	107.0(17)	C8S-C9S-C10S	114.79(17)
C8S-C9S-H9C	108.6	C10S-C9S-H9C	108.6
C8S-C9S-H9D	108.6	C10S-C9S-H9D	108.6
H9C-C9S-H9D	107.5	C9S-C10S-C11S	115.14(19)
C9S-C10S-H10C	108.5	C11S-C10S-H10C	108.5
C9S-C10S-H10D	108.5	C11S-C10S-H10D	108.5
H10C-C10S-H10D	107.5	C10S-C11S-C12S	112.7(2)
C10S-C11S-H11C	109.1	C12S-C11S-H11C	109.1
C10S-C11S-H11D	109.1	C12S-C11S-H11D	109.1
H11C-C11S-H11D	107.8	C8S-C9T-C10T	115.3(11)
C8S-C9T-H9E	108.5	C10T-C9T-H9E	108.5
C8S-C9T-H9F	108.5	C10T-C9T-H9F	108.5
H9E-C9T-H9F	107.5	C8S-C9T-H8D	41.3(9)
C10T-C9T-H8D	134.8(14)	H9E-C9T-H8D	115.6
H9F-C9T-H8D	67.6	C9T-C10T-C11T	109.8(14)
C9T-C10T-H10E	109.7		
C11T-C10T-H10E	109.7	C9T-C10T-H10F	109.7
C11T-C10T-H10F	109.7	H10E-C10T-H10F	108.2
C12T-C11T-C10T	110.0(15)	C12T-C11T-H11E	109.7
C10T-C11T-H11E	109.7	C12T-C11T-H11F	109.7
C10T-C11T-H11F	109.7	H11E-C11T-H11F	108.2
C11T-C12T-H12G	109.5	C11T-C12T-H12H	109.5
H12G-C12T-H12H	109.5	C11T-C12T-H12I	109.5
H12G-C12T-H12I	109.5	H12H-C12T-H12I	109.5

5.5. 2-Propyl-perhydro-6-azulenecarboxylic acid (73)



Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 5256.6(7) pm	α= 90°
	b = 1072.13(14) pm	β= 91.383(3)°
	c = 2265.5(3) pm	γ = 90°
Volume, Z	1.2764(3) nm^3, 4	

Bond lengths [A]

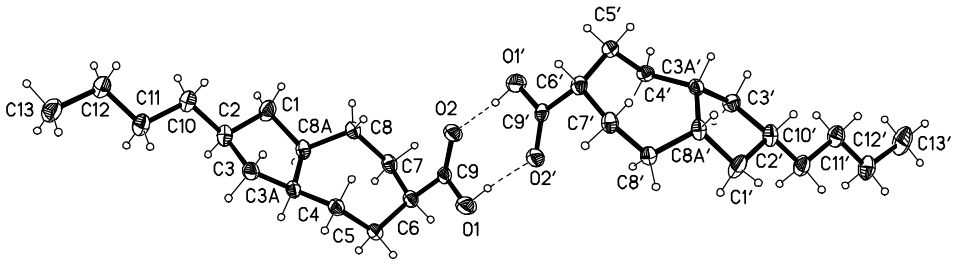
C(1)-C(2)	1.5301(11)	C(1)-C(8A)	1.5388(10)
C(2)-C(10)	1.5288(10)	C(2)-C(3)	1.5314(11)
C(3)-C(3A)	1.5434(10)	C(3A)-C(4)	1.5286(10)
C(3A)-C(8A)	1.5676(11)	C(4)-C(5)	1.5346(10)
C(5)-C(6)	1.5328(11)	C(6)-C(9)	1.5169(11)
C(6)-C(7)	1.5364(12)	C(7)-C(8)	1.5336(11)
C(8)-C(8A)	1.5330(11)	C(9)-O(2)	1.2215(10)
C(9)-O(1)	1.3218(10)	C(10)-C(11)	1.5232(11)
C(11)-C(12)	1.5263(12)		

Bond angles [°]

C(2)-C(1)-C(8A)	106.32(6)	C(10)-C(2)-C(1)	113.12(6)
C(10)-C(2)-C(3)	114.89(6)	C(1)-C(2)-C(3)	101.46(6)
C(2)-C(3)-C(3A)	106.21(6)	C(4)-C(3A)-C(3)	112.00(6)
C(4)-C(3A)-C(8A)	116.49(6)	C(3)-C(3A)-C(8A)	105.26(6)
C(3A)-C(4)-C(5)	114.70(6)	C(6)-C(5)-C(4)	115.41(6)
C(9)-C(6)-C(5)	110.62(7)	C(9)-C(6)-C(7)	112.86(7)

C(5)-C(6)-C(7)	115.51(7)	C(8)-C(7)-C(6)	115.47(6)
C(8A)-C(8)-C(7)	115.42(7)	C(8)-C(8A)-C(1)	111.52(6)
C(8)-C(8A)-C(3A)	117.61(6)	C(1)-C(8A)-C(3A)	104.91(6)
O(2)-C(9)-O(1)	122.10(8)	O(2)-C(9)-C(6)	123.60(7)
O(1)-C(9)-C(6)	114.23(7)	C(11)-C(10)-C(2)	115.16(7)
C(10)-C(11)-C(12)	111.85(7)		

5.6. 2-Butyl-perhydro-6-azulenecarboxylic acid (74)



Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 5217.1(8) nm	α= 90°
	b = 2236.2(3) nm	β= 90.278(4)°
	c = 2389.3(3) nm	γ = 90°
Volume, Z	2.7875(7) nm^3, 8	

Bond lengths [A]

C(1)-C(2)	1.5269(18)	C(1)-C(8A)	1.5336(18)
C(2)-C(10)	1.5235(17)	C(2)-C(3)	1.5273(17)
C(3)-C(3A)	1.5394(16)	C(3A)-C(4)	1.5279(16)
C(3A)-C(8A)	1.5624(17)	C(4)-C(5)	1.5351(16)
C(5)-C(6)	1.5382(17)	C(6)-C(9)	1.5169(15)
C(6)-C(7)	1.5289(18)	C(7)-C(8)	1.5300(16)
C(8)-C(8A)	1.5273(15)	C(9)-O(2)	1.2164(15)
C(9)-O(1)	1.3176(15)	C(10)-C(11)	1.5226(18)
C(11)-C(12)	1.5209(18)	C(12)-C(13)	1.5216(19)
C(1')-C(2')	1.5237(17)	C(1')-C(8A')	1.5324(17)
C(2')-C(10')	1.5230(17)	C(2')-C(3')	1.5234(16)
C(3')-C(3A')	1.5355(15)	C(3A')-C(4')	1.5236(15)
C(3A')-C(8A')	1.5576(17)	C(4')-C(5')	1.5309(15)
C(5')-C(6')	1.5339(16)	C(6')-C(9')	1.5142(16)
C(6')-C(7')	1.5319(17)	C(7')-C(8')	1.5309(16)
C(8')-C(8A')	1.5289(15)	C(9')-O(2')	1.2223(15)
C(9')-O(1')	1.3186(14)	C(10')-C(11')	1.5247(18)
C(11')-C(12')	1.5217(18)	C(12')-C(13')	1.518(2)

Bond angles [°].

C(2)-C(1)-C(8A)	105.59(11)	C(10)-C(2)-C(1)	113.71(11)
C(10)-C(2)-C(3)	116.65(10)	C(1)-C(2)-C(3)	100.73(9)

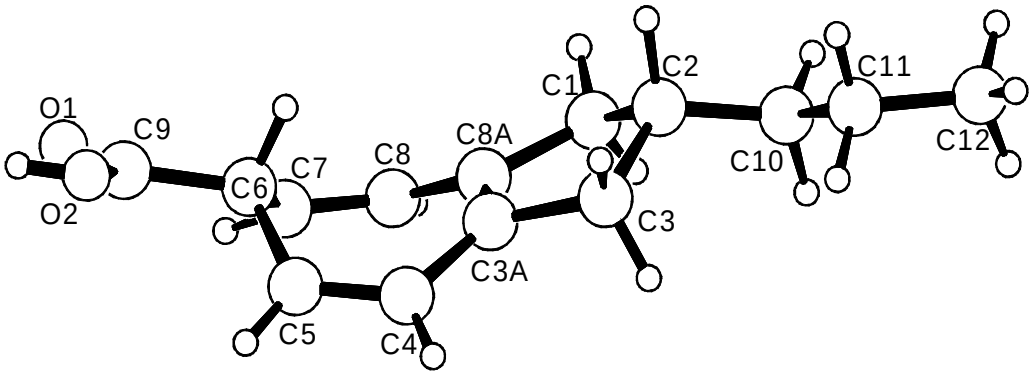
C(2)-C(3)-C(3A)	105.10(9)	C(4)-C(3A)-C(3)	112.91(9)
C(4)-C(3A)-C(8A)	116.93(9)	C(3)-C(3A)-C(8A)	105.14(9)
C(3A)-C(4)-C(5)	114.75(10)	C(4)-C(5)-C(6)	115.63(10)
C(9)-C(6)-C(7)	111.54(10)	C(9)-C(6)-C(5)	111.43(10)
C(7)-C(6)-C(5)	115.26(9)	C(6)-C(7)-C(8)	116.61(10)
C(8A)-C(8)-C(7)	115.70(10)	C(8)-C(8A)-C(1)	111.58(10)
C(8)-C(8A)-C(3A)	117.65(9)	C(1)-C(8A)-C(3A)	104.64(9)
O(2)-C(9)-O(1)	122.46(11)	O(2)-C(9)-C(6)	123.64(11)
O(1)-C(9)-C(6)	113.85(10)	C(11)-C(10)-C(2)	115.56(11)
C(12)-C(11)-C(10)	112.83(11)	C(11)-C(12)-C(13)	113.64(12)
C(2')-C(1')-C(8A')	105.91(11)	C(10')-C(2')-C(3')	116.57(10)
C(10')-C(2')-C(1')	114.13(11)	C(3')-C(2')-C(1')	100.72(9)
C(2')-C(3')-C(3A')	104.88(9)	C(4')-C(3A')-C(3')	112.79(9)
C(4')-C(3A')-C(8A')	117.19(9)	C(3')-C(3A')-C(8A')	105.32(9)
C(3A')-C(4')-C(5')	114.11(9)	C(4')-C(5')-C(6')	115.14(10)
C(9')-C(6')-C(7')	111.48(10)	C(9')-C(6')-C(5')	110.98(9)
C(7')-C(6')-C(5')	115.89(9)	C(8')-C(7')-C(6')	116.53(9)
C(8A')-C(8')-C(7')	114.90(10)	C(8')-C(8A')-C(1')	112.26(10)
C(8')-C(8A')-C(3A')	117.31(9)	C(1')-C(8A')-C(3A')	104.47(9)
O(2')-C(9')-O(1')	122.10(11)	O(2')-C(9')-C(6')	124.44(11)
O(1')-C(9')-C(6')	113.43(11)	C(2')-C(10')-C(11')	114.92(11)
C(12')-C(11')-C(10')	112.44(12)	C(13')-C(12')-C(11')	114.01(13)

Torsion angles [°]

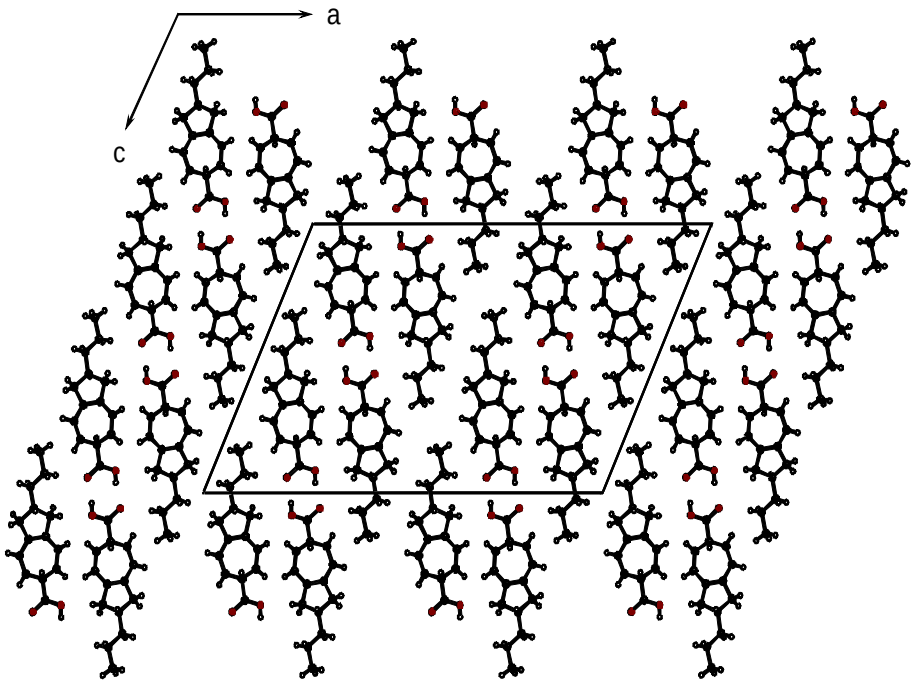
C(8A)-C(1)-C(2)-C(10)	167.28(10)	C(8A)-C(1)-C(2)-C(3)	41.70(12)
C(10)-C(2)-C(3)-C(3A)	-164.88(10)	C(1)-C(2)-C(3)-C(3A)	-41.30(12)
C(2)-C(3)-C(3A)-C(4)	154.31(10)	C(2)-C(3)-C(3A)-C(8A)	25.73(11)
C(3)-C(3A)-C(4)-C(5)	171.53(10)	C(8A)-C(3A)-C(4)-C(5)	-66.28(13)
C(3A)-C(4)-C(5)-C(6)	84.45(12)	C(4)-C(5)-C(6)-C(9)	68.75(13)
C(4)-C(5)-C(6)-C(7)	-59.66(13)	C(9)-C(6)-C(7)-C(8)	-70.80(12)
C(5)-C(6)-C(7)-C(8)	57.56(14)	C(6)-C(7)-C(8)-C(8A)	-81.05(13)
C(7)-C(8)-C(8A)-C(1)	-171.85(10)	C(7)-C(8)-C(8A)-C(3A)	67.22(13)
C(2)-C(1)-C(8A)-C(8)	-154.40(10)	C(2)-C(1)-C(8A)-C(3A)	-26.15(12)
C(4)-C(3A)-C(8A)-C(8)	-1.46(15)	C(3)-C(3A)-C(8A)-C(8)	124.68(10)
C(4)-C(3A)-C(8A)-C(1)	-125.93(11)	C(3)-C(3A)-C(8A)-C(1)	0.21(11)
C(7)-C(6)-C(9)-O(2)	-0.92(16)	C(5)-C(6)-C(9)-O(2)	-131.30(12)
C(7)-C(6)-C(9)-O(1)	-178.50(10)	C(5)-C(6)-C(9)-O(1)	51.12(13)
C(1)-C(2)-C(10)-C(11)	177.19(11)	C(3)-C(2)-C(10)-C(11)	-66.20(14)

C(2)-C(10)-C(11)-C(12)	-174.96(11)	C(10)-C(11)-C(12)-C(13)	178.78(11)
C(8A')-C(1')-C(2')-C(10')	-166.80(10)	C(8A')-C(1')-C(2')-C(3')	-41.09(12)
C(10')-C(2')-C(3')-C(3A')	165.68(10)	C(1')-C(2')-C(3')-C(3A')	41.63(12)
C(2')-C(3')-C(3A')-C(4')	-155.98(10)	C(2')-C(3')-C(3A')-C(8A')	-27.00(11)
C(3')-C(3A')-C(4')-C(5')	-170.78(10)	C(8A')-C(3A')-C(4')-C(5')	66.67(13)
C(3A')-C(4')-C(5')-C(6')	-85.11(12)	C(4')-C(5')-C(6')-C(9')	-69.03(12)
C(4')-C(5')-C(6')-C(7')	59.43(13)	C(9')-C(6')-C(7')-C(8')	71.61(12)
C(5')-C(6')-C(7')-C(8')	-56.61(14)	C(6')-C(7')-C(8')-C(8A')	80.55(12)
C(7')-C(8')-C(8A')-C(1')	170.31(10)	C(7')-C(8')-C(8A')-C(3A')	-68.67(13)
C(2')-C(1')-C(8A')-C(8')	152.88(10)	C(2')-C(1')-C(8A')-C(3A')	24.73(12)
C(4')-C(3A')-C(8A')-C(8')	2.75(15)	C(3')-C(3A')-C(8A')-C(8')	-123.57(10)
C(4')-C(3A')-C(8A')-C(1')	127.75(11)	C(3')-C(3A')-C(8A')-C(1')	1.43(12)
C(7')-C(6')-C(9')-O(2')	1.15(16)	C(5')-C(6')-C(9')-O(2')	131.95(12)
C(7')-C(6')-C(9')-O(1')	179.32(9)	C(5')-C(6')-C(9')-O(1')	-49.89(13)
C(3')-C(2')-C(10')-C(11')	67.98(14)	C(1')-C(2')-C(10')-C(11')	-175.15(11)
C(2')-C(10')-C(11')-C(12')	176.47(11)	C(10')-C(11')-C(12')-C(13')	-176.00(11)

5.7. 2-Propyl-1, 2, 3, 6-tetrahydro-azulene-6-carboxylic acid (70)



Molecular structure of **70.** Only one of the three disordered positions of the carboxyl group is shown.



Packing arrangement of **70**. View along the crystallographic b-axis.

Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 31154(3) nm	α= 90°
	b = 4370.6(4) nm	β= 114.919(2)°
	c = 20266(2) nm	γ = 90°
Volume, Z	2.5026(4) nm^3, 8	

Bond lengths [A]

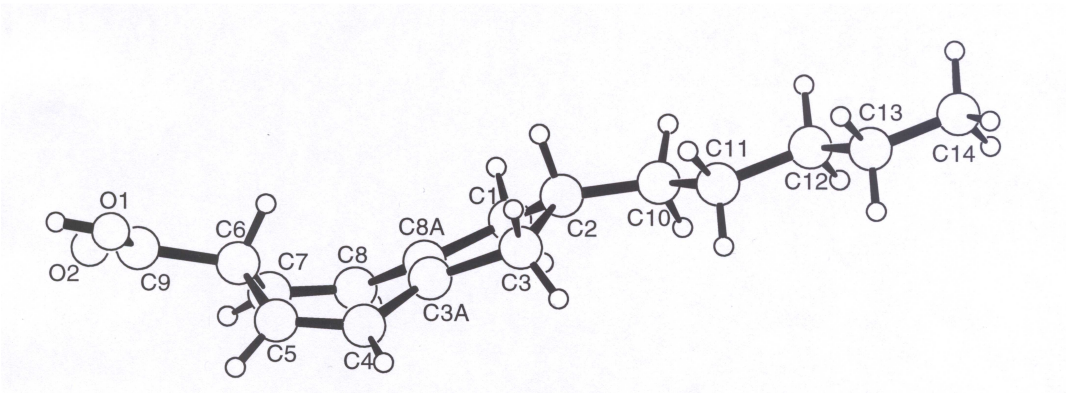
O1-C9	1.274(3)	O2-C9	1.294(3)
O2-H2	0.8200	O1A-C9	1.230(8)
O2A-C9	1.282(9)	O2A-H2A	0.8200
O1B-C9	1.253(8)	O2B-C9	1.259(8)
O2B-H2B	0.8200	C1-C8A	1.499(2)
C1-C2	1.529(3)	C1-H1A	1.01(2)
C1-H1B	0.94(2)	C2-C10	1.516(2)
C2-C3	1.529(2)	C2-H2	1.07(2)
C3-C3A	1.506(2)	C3-H3A	1.03(2)
C3-H3B	1.03(2)	C3A-C8A	1.356(2)
C3A-C4	1.443(2)	C4-C5	1.334(2)
C4-H4	0.95(2)	C5-C6	1.501(2)
C5-H5	0.97(2)	C6-C7	1.499(2)
C6-C9	1.499(2)	C6-H6	1.02(2)
C7-C8	1.328(2)	C7-H7	0.98(2)
C8-C8A	1.437(2)	C8-H8	0.96(2)
C10-C11	1.508(3)	C10-H10A	0.98(2)
C10-H10B	1.02(2)	C11-C12	1.495(4)
C11-C12A	1.598(15)	C11-H11A	1.04(2)
C11-H11B	0.97(2)	C12-H12A	0.9600
C12-H12B	0.9600	C12-H12C	0.9600
C12A-H12D	0.9600	C12A-H12E	0.9600
C12A-H12F	0.9600		

Bond angles [°].

C9-O2-H2	109.5	C9-O2A-H2A	109.5
C9-O2B-H2B	109.5	C8A-C1-C2	104.62(13)
C8A-C1-H1A	111.8(13)	C2-C1-H1A	111.7(13)
C8A-C1-H1B	109.8(13)	C2-C1-H1B	114.2(13)
H1A-C1-H1B	104.8(19)	C10-C2-C1	113.99(15)
C10-C2-C3	116.25(14)	C1-C2-C3	104.77(14)
C10-C2-H2	103.6(12)	C1-C2-H2	110.7(12)
C3-C2-H2	107.4(11)	C3A-C3-C2	104.22(13)
C3A-C3-H3A	111.9(11)	C2-C3-H3A	108.7(12)
C3A-C3-H3B	107.4(12)	C2-C3-H3B	110.8(13)
H3A-C3-H3B	113.3(18)	C8A-C3A-C4	125.40(14)
C8A-C3A-C3	110.94(13)	C4-C3A-C3	123.09(13)
C5-C4-C3A	124.27(15)	C5-C4-H4	118.6(12)
C3A-C4-H4	117.1(12)	C4-C5-C6	120.55(14)
C4-C5-H5	118.5(12)	C6-C5-H5	120.9(12)

C7-C6-C9	113.68(13)	C7-C6-C5	108.28(14)
C9-C6-C5	113.08(14)	C7-C6-H6	107.2(11)
C9-C6-H6	105.9(11)	C5-C6-H6	108.4(11)
C8-C7-C6	120.18(15)	C8-C7-H7	122.9(12)
C6-C7-H7	116.9(12)	C7-C8-C8A	124.60(16)
C7-C8-H8	120.5(13)	C8A-C8-H8	114.9(13)
C3A-C8A-C8	125.71(15)	C3A-C8A-C1	110.65(13)
C8-C8A-C1	122.90(14)	O1A-C9-O1B	62.8(5)
O1A-C9-O2B	88.9(5)	O1B-C9-O2B	123.4(5)
O1A-C9-O1	30.5(3)	O1B-C9-O1	33.1(3)
O2B-C9-O1	111.5(4)	O1A-C9-O2A	122.8(5)
O1B-C9-O2A	91.6(5)	O2B-C9-O2A	62.7(4)
O1-C9-O2A	114.5(4)	O1A-C9-O2	114.4(4)
O1B-C9-O2	115.1(4)	O2B-C9-O2	33.2(3)
O1-C9-O2	124.4(2)	O2A-C9-O2	30.9(3)
O1A-C9-C6	122.4(4)	O1B-C9-C6	115.5(4)
O2B-C9-C6	121.0(4)	O1-C9-C6	119.59(18)
O2A-C9-C6	114.8(4)	O2-C9-C6	115.87(17)
C11-C10-C2	115.98(17)	C11-C10-H10A	108.8(12)
C2-C10-H10A	110.0(12)	C11-C10-H10B	109.4(12)
C2-C10-H10B	109.8(12)	H10A-C10-H10B	101.9(17)
C12-C11-C10	116.3(3)	C12-C11-C12A	17.0(5)
C10-C11-C12A	103.5(5)	C12-C11-H11A	109.4(13)
C10-C11-H11A	110.6(13)	C12A-C11-H11A	106.6(14)
C12-C11-H11B	101.8(14)	C10-C11-H11B	112.0(14)
C12A-C11-H11B	118.2(14)	H11A-C11-H11B	105.9(19)
C11-C12-H12A	109.5	C11-C12-H12B	109.5
C11-C12-H12C	109.5	C1-C12A-H12D	109.5
C11-C12A-H12E	109.5	H12D-C12A-H12E	109.5
C11-C12A-H12F	109.5	H12D-C12A-H12F	109.5
H12E-C12A-H12F	109.		

5.8. 2-Pentyl-1, 2, 3, 6-tetrahydro-azulene-6-carboxylic acid (72)



Molecular structure of **72.** Only one of the both disordered positions of C2 is shown.

Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16201(4) nm	α= 90°
	b = 4589(1) nm	β= 114.919(2)°
	c = 19159(5) nm	γ = 90°
Volume, Z	1.4122(6) nm^3, 4	

Bond lengths [A]

O1-C9	1.296 (9)	O1-H1	0.8400
O2-C9	1.199 (9)	C1-C2	1.439 (17)
C1-C8A	1.520 (10)	C1-C2A	1.60 (2)
C1-H1A	0.9900	C1-H1B	0.9900
C2-C10	1.471 (19)	C2-C3	1.543 (19)
C2-H2	1.0000	C2A-C3	1.339 (19)
C2A-C10	1.56 (2)	C2A-H2A	1.0000
C3-C3A	1.534 (11)	C3-H3A	0.9900
C3-H3B	0.9900	C3A-C8A	1.319 (10)
C3A-C4	1.438 (11)	C4-C5	1.336 (11)
C4-H4	0.9500	C5-C6	1.460 (10)
C5-H5	0.96 (8)	C6-C7	1.492 (10)
C6-C9	1.510 (10)	C6-H6	1.0000
C7-C8	1.322 (9)	C7-H7	0.9500
C8-C8A	1.438 (10)	C8-H8	0.9500
C10-C11	1.464 (11)	C10-H10A	0.9900
C10-H10B	0.9900	C11-C12	1.500 (11)
C11-H11A	0.9900	C11-H11B	0.9900
C12-C13	1.445 (11)	C12-H12A	0.9900
C12-H12B	0.9900	C13-C14	1.432 (10)

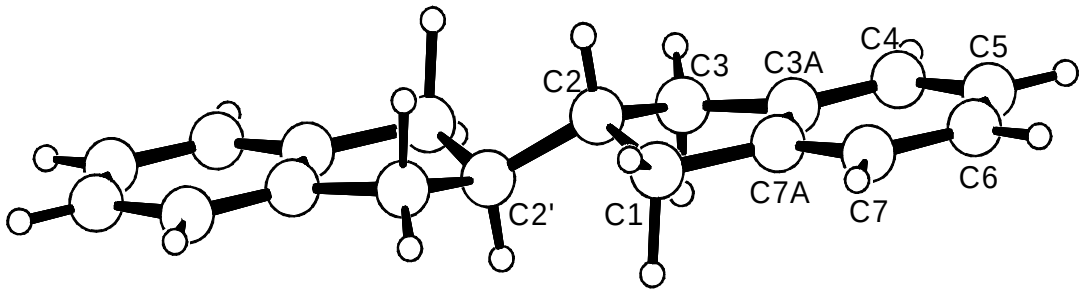
C13-C13A	0.9900	C13-C13B	0.9900
C14-H14A	0.9800	C14-H14B	0.9800
C14-H14C	0.9800		

Bond angles [°].

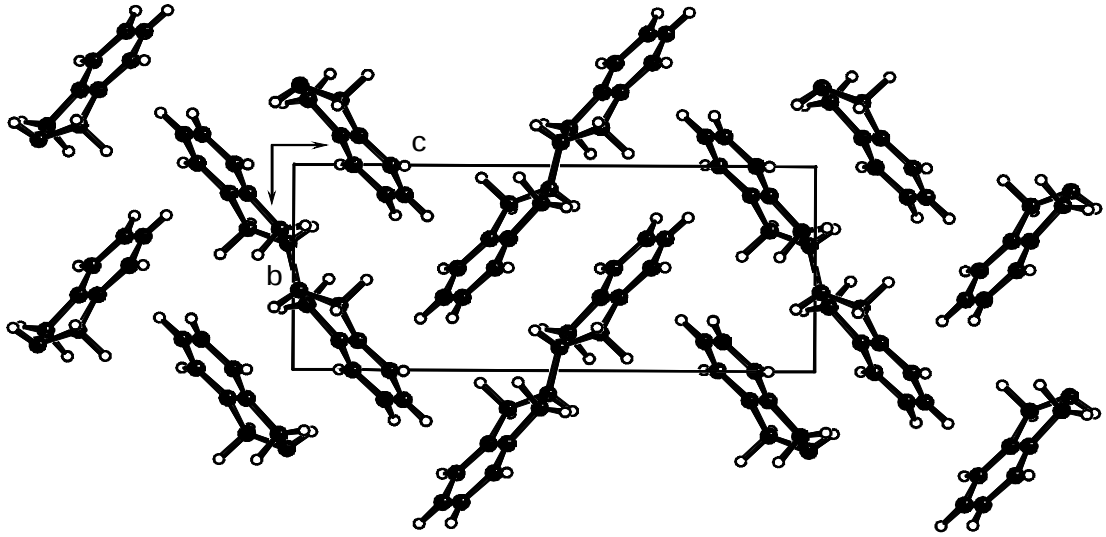
C9-O1-H1	109.5	C2-C1-C8A	107.3 (9)
C2-C1-C2A	25.7 (10)	C8A-C1-C2A	99.5 (9)
C2-C1-H1A	110.3	C8A-C1-H1A	110.3
C2A-C1-H1A	91.2	C2-C1-H1B	110.3
C8A-C1-H1B	110.3	C8A-C1-H1B	110.3
C2A-C1-H1B	134.8	H1A-C1-H1B	108.5
C1-C2-C10	124.0 (13)	C1-C2-C3	105.0 (12)
C10-C2-C3	118.7 (13)	C1-C2-H2	101.7
C10-C2-H2	101.7	C3-C2-H2	101.7
C3-C2A-C10	126.9 (15)	C3-C2A-C1	107.2 (13)
C10-C2A-C1	109.1 (14)	C3-C2A-H2A	103.7
C10-C2A-H2A	103.7	C1-C2A-H2A	103.7
C2A-C3-C3A	106.1 (10)	C2A-C3-C2	26.6 (11)
C3A-C3-C2	104.6 (9)	C2A-C3-H3A	86.0
C3A-C3-H3A	110.8	C2-C3-H3A	110.8
C2A-C3-H3B	131.0	C3A-C3-H3B	110.8
C2-C3-H3B	110.8	H3A-C3-H3B	108.9
C8A-C3A-C4	124.5 (8)	C8A-C3A-C3	109.3 (9)
C4-C3A-C3	125.9 (10)	C5-C4-C3A	123.5 (8)
C5-H4-H4	118.2	C3A-C4-H4	118.2
C4-C5-C6	122.9 (8)	C4-C5-H5	122 (5)
C6-C5-H5	111 (5)	C5-C6-C7	109.5 (7)
C5-C6-C9	115.3 (7)	C7-C6-C9	114.1 (8)
C5-C6-H6	105.7	C7-C6-H6	105.7
C9-C6-H6	105.7	C8-C7-C6	129.9 (7)
C8-C7-H7	119.5	C6-C7-H7	119.5
C7-C8-C8A	123.7 (7)	C7-C8-H8	118.1
C8A-C8-H8	118.1	C3A-C8A-C8	127.4 (8)
C3A-C8A-C1	110.8 (8)	C8-C8A-C1	121.2 (9)
O2-C9-O1	123.2 (8)	O2-C9-C6	123.3 (8)
O1-C9-C6	113.4 (9)	C11-C10-C2	125.7 (10)
C11-C10-C2A	115.4 (10)	C2-C10-C2A	26.3 (10)
C11-C10-H10A	105.9	C2-C10-H10A	105.9

C2A-C10-H10A	88.1	C11-C10-H10B	105.9
C2-C10-H10B	105.9	C2A-C10-H10B	130.5
H10A-C10-H10B	106.2	C10-C11-C12	117.8 (8)
C10-C11-H11A	107.9	C12-C11-H11A	107.9
C10-C11-H11B	107.9	C12-C11-H11B	107.9
H11A-C11-H11B	107.2	C13-C12-C11	118.8 (8)
C13-C12-H12A	107.6	C11-C12-H12A	107.6
C13-C12-H12B	107.6	C11-C12-H12B	107.6
H12A-C12-H12B	107.0	C14-C13-C12	120.0 (8)
C14-C13-H13A	107.3	C12-C13-H13A	107.3
C14-C13-H13B	107.3	C12-C13-H13B	107.3
H13A-C13-H13B	106.9	C13-C14-H14A	109.5
C13-C14-H14B	109.5	H14A-C14-H14B	109.5
C13-C14-H14C	109.5	H14A-C14-H14C	109.5
H14B-C14-H14C	109.5		

5.9. 2, 3, 2', 3', Tetrahydro-1*H*, 1'*H*-[2, 2'] biindenyl (43)



Molecular structure of **43**. It is shown only one of two disordered positions of C2



Packing arrangement of **43**. View along the crystallographic a-axis.

Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 6296.6(7) nm	α= 90°
	b = 6607.1(7) nm	β= 95.051(2)°
	c = 15516(2) nm	γ = 90°
Volume, Z	0.6430(1) nm^3, 2	

Bond lengths [A]

C1-C2A	1.492(3)	C1-C7A	1.5087(13)
C1-C2	1.520(3)	C1-H1A	1.00(2)
C1-H1B	1.18(2)	C1-H1C	0.95(3)
C1-H1D	1.14(3)	C3-C2A	1.492(3)
C3-C3A	1.5096(13)	C3-C2	1.519(3)
C3-H3A	0.96(2)	C3-H3B	1.16(2)
C3-H3C	0.93(3)	C3-H3D	1.20(4)

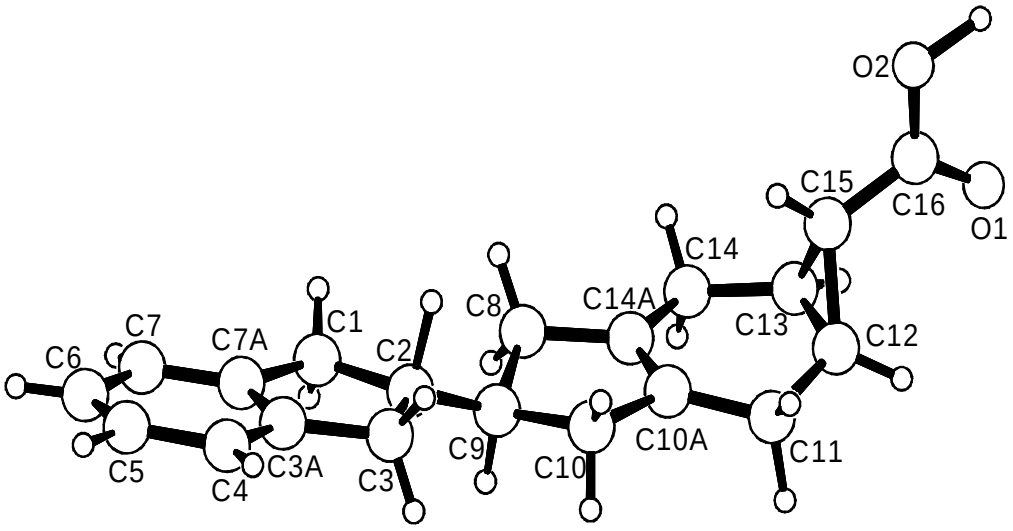
C2-C2A	0.518(3)	C2-C2A#1	1.420(2)
C2-C2#1	1.546(6)	C2-H2	0.96(2)
C2A-C2#1	1.420(2)	C2A-C2A#1	1.477(6)
C2A-H2	1.48(2)	C2A-H2A	1.06(4)
C3A-C4	1.3901(12)	C3A-C7A	1.3957(13)
C4-C5	1.3941(13)	C4-H4	1.016(14)
C5-C6	1.3865(15)	C5-H5	1.001(15)
C6-C7	1.3965(13)	C6-H6	0.991(16)
C7-C7A	1.3893(12)	C7-H7	0.987(12)

Bond angles [°].

C2A-C1-C7A	104.57(14)	C2A-C1-C2	19.76(10)
C7A-C1-C2	103.92(13)	C2A-C1-H1A	133.2(13)
C7A-C1-H1A	116.8(13)	C2-C1-H1A	121.7(14)
C2A-C1-H1B	88.4(11)	C7A-C1-H1B	103.3(11)
C2-C1-H1B	107.6(11)	H1A-C1-H1B	101.8(17)
C2A-C1-H1C	123.3(18)	C7A-C1-H1C	120.0(17)
C2-C1-H1C	133.5(17)	H1A-C1-H1C	51.2(19)
H1B-C1-H1C	50.6(19)	C2A-C1-H1D	101.8(16)
C7A-C1-H1D	105.4(17)	C2-C1-H1D	83.1(16)
H1A-C1-H1D	48.2(18)	H1B-C1-H1D	145.9(19)
H1C-C1-H1D	98(2)	C2A-C3-C3A	104.65(14)
C2A-C3-C2	19.77(10)	C3A-C3-C2	104.09(13)
C2A-C3-H3A	133.6(14)	C3A-C3-H3A	115.2(14)
C2-C3-H3A	121.2(15)	C2A-C3-H3B	88.5(11)
C3A-C3-H3B	104.4(11)	C2-C3-H3B	107.5(11)
H3A-C3-H3B	103.0(18)	C2A-C3-H3C	128.4(17)
C3A-C3-H3C	118.3(17)	C2-C3-H3C	136.7(16)
H3A-C3-H3C	47.8(19)	H3B-C3-H3C	55.6(19)
C2A-C3-H3D	100.4(16)	C3A-C3-H3D	103.8(17)
C2-C3-H3D	81.4(16)	H3A-C3-H3D	48.9(19)
H3B-C3-H3D	147(2)	H3C-C3-H3D	96(2)
C2A-C2-C2A#1	85.9(7)	C2A-C2-C3	77.2(6)
C2A#1-C2-C3	122.52(18)	C2A-C2-C1	77.1(6)
C3-C2-C1	106.48(18)	C2A-C2-C2#1	66.4(6)
C2A#1-C2-C2#1	19.51(14)	C3-C2-C2#1	114.8(3)
C1-C2-C2#1	114.8(3)	C2A-C2-H2	177.6(15)
C2A#1-C2-H2	91.7(13)	C3-C2-H2	104.6(11)

C1-C2-H2	103.8(12)	C2#1-C2-H2	111.2(13)
C2A-C2-H2A	1.2(14)	C2A#1-C2-H2A	85.3(14)
C3-C2-H2A	78.3(13)	C1-C2-H2A	76.6(13)
C2#1-C2-H2A	65.8(14)	H2-C2-H2A	176.7(18)
C2-C2A-C2#1	94.1(7)	C2-C2A-C2A#1	73.6(6)
C2#1-C2A-C2A#1	20.47(11)	C2-C2A-C3	83.1(6)
C2#1-C2A-C3	124.90(17)	C2A#1-C2A-C3	120.5(3)
C2-C2A-C1	83.2(6)	C2#1-C2A-C1	125.00(17)
C2A#1-C2A-C1	120.7(3)	C3-C2A-C1	109.3(2)
C2-C2A-H2	1.6(9)	C2#1-C2A-H2	92.6(8)
C2A#1-C2A-H2	72.1(8)	C3-C2A-H2	84.2(8)
C1-C2A-H2	83.8(8)	C2-C2A-H2A	178(2)
C2#1-C2A-H2A	85(2)	C2A#1-C2A-H2A	106(2)
C3-C2A-H2A	98.7(19)	C1-C2A-H2A	96(2)
H2-C2A-H2A	177(2)	C4-C3A-C7A	120.42(8)
C4-C3A-C3	129.57(9)	C7A-C3A-C3	110.00(8)
C3A-C4-C5	118.99(9)	C3A-C4-H4	121.3(8)
C5-C4-H4	119.7(7)	C6-C5-C4	120.71(8)
C6-C5-H5	119.4(8)	C4-C5-H5	119.9(8)
C5-C6-C7	120.33(8)	C5-C6-H6	120.5(8)
C7-C6-H6	119.1(8)	C7A-C7-C6	119.09(9)
C7A-C7-H7	119.9(7)	C6-C7-H7	121.0(7)
C7-C7A-C3A	120.46(8)	C7-C7A-C1	129.26(9)
C3A-C7A-C1	110.26(8)		

5.10. 9-Indan-2-yl-15, 13, 14, 8, 9, 10, 11, 12-octahydro-cyclopropa[*f*]indene-15-carboxylic acid (131)



Molecular structure of **131**. It is shown only one of the disordered positions of C9

Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8192(1) nm	α= 97.169(3)°
	b = 9160(1) nm	β= 95.168(3)°
	c = 1135(2) nm	γ = 110.853(3)°
Volume, Z	0.7813(2) nm^3, 2	

Bond lengths [A]

O1-C16	1.228(3)	O2-C16	1.320(3)
O2-H1	1.12(4)	C1-C2	1.492(5)
C1-C7A	1.500(4)	C1-H1A	0.87(4)
C1-H1B	0.95(4)	C2-C9A	1.360(9)
C2-C9	1.473(9)	C2-C3	1.496(4)
C2-H2	1.18(6)	C2-H2A	1.37(5)
C3-C3A	1.499(4)	C3-H3A	0.99(4)
C3-H3B	0.93(4)	C3A-C7A	1.385(4)
C3A-C4	1.404(4)	C4-C5	1.411(4)
C4-H4	0.94(3)	C5-C6	1.381(4)
C5-H5	0.98(3)	C6-C7	1.397(4)
C6-H6	0.97(3)	C7-C7A	1.394(4)
C7-H7	0.92(3)	C8-C14A	1.498(4)
C8-C9	1.500(9)	C8-C9A	1.599(9)
C8-H8A	1.00(3)	C8-H8B	0.93(3)
C9-C10	1.553(9)	C9-H9	1.0000
C9A-C10	1.538(10)	C9A-H9A	1.0000
C9A-H2	1.40(5)	C10-C10A	1.497(4)

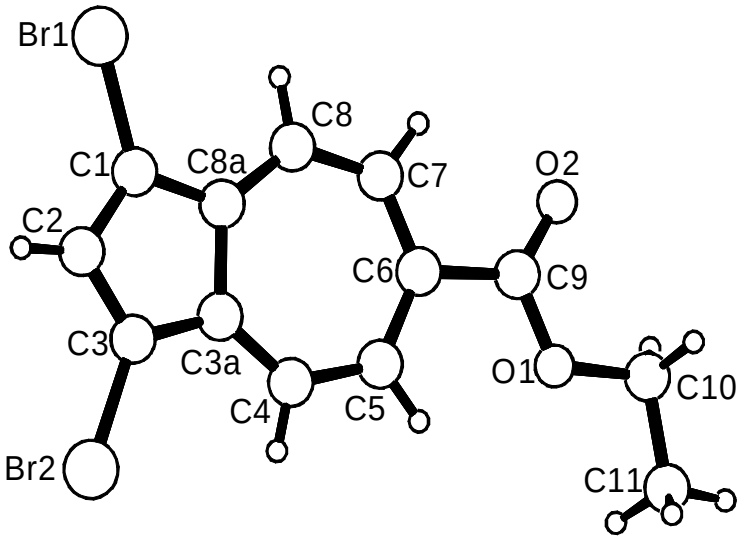
C10-H10A	0.94(3)	C10-H10B	1.02(4)
C10A-C14A	1.335(4)	C10A-C11	1.484(4)
C11-C12	1.515(4)	C11-H11A	0.98(2)
C11-H11B	1.06(3)	C12-C13	1.486(4)
C12-C15	1.524(4)	C12-H12	0.99(2)
C13-C14	1.518(4)	C13-C15	1.522(4)
C13-H13	1.00(2)	C14-C14A	1.494(4)
C14-H14A	1.02(2)	C14-H14B	0.98(3)
C15-C16	1.468(4)	C15-H15	0.97(3)

Bond angles [°].

C16-O2-H1	108.0(17)	C2-C1-C7A	105.4(3)
C2-C1-H1A	110(2)	C7A-C1-H1A	113(2)
C2-C1-H1B	113(3)	C7A-C1-H1B	117(3)
H1A-C1-H1B	98(3)	C9A-C2-C9	30.0(3)
C9A-C2-C1	127.8(5)	C9-C2-C1	120.9(4)
C9A-C2-C3	121.6(5)	C9-C2-C3	126.8(4)
C1-C2-C3	108.7(3)	C9A-C2-H2	67(3)
C9-C2-H2	96(3)	C1-C2-H2	96(3)
C3-C2-H2	97(2)	C9A-C2-H2A	98(2)
C9-C2-H2A	68(2)	C1-C2-H2A	91.4(19)
C3-C2-H2A	94(2)	H2-C2-H2A	164(3)
C2-C3-C3A	105.1(3)	C2-C3-H3A	107(2)
C3A-C3-H3A	115(2)	C2-C3-H3B	111(2)
C3A-C3-H3B	112(2)	H3A-C3-H3B	107(3)
C7A-C3A-C4	120.6(3)	C7A-C3A-C3	110.5(2)
C4-C3A-C3	128.9(3)	C3A-C4-C5	118.2(3)
C3A-C4-H4	123.5(18)	C5-C4-H4	118.0(18)
C6-C5-C4	120.4(3)	C6-C5-H5	117.2(17)
C4-C5-H5	122.0(17)	C5-C6-C7	120.9(3)
C5-C6-H6	117.7(15)	C7-C6-H6	121.2(15)
C7A-C7-C6	118.6(3)	C7A-C7-H7	117.7(19)
C6-C7-H7	121.9(19)	C3A-C7A-C7	120.9(3)
C3A-C7A-C1	110.2(2)	C7-C7A-C1	128.9(3)
C14A-C8-C9	104.4(4)	C14A-C8-C9A	103.9(4)
C9-C8-C9A	27.5(3)	C14A-C8-H8A	112.4(18)
C9-C8-H8A	125.2(18)	C9A-C8-H8A	102.6(18)
C14A-C8-H8B	113.6(19)	C9-C8-H8B	101(2)
C9A-C8-H8B	124(2)	H8A-C8-H8B	100(3)
C2-C9-C8	119.4(6)	C2-C9-C10	115.0(5)
C8-C9-C10	105.3(5)	C2-C9-H9	105.3
C8-C9-H9	105.3	C10-C9-H9	105.3
C2-C9A-C10	123.3(7)	C2-C9A-C8	120.1(6)
C10-C9A-C8	101.4(5)	C2-C9A-H9A	103.0
C10-C9A-H9A	103.0	C8-C9A-H9A	103.0
C2-C9A-H2	50(2)	C10-C9A-H2	135(2)
C8-C9A-H2	120(2)	H9A-C9A-H2	53.1
C10A-C10-C9A	105.7(4)	C10A-C10-C9	103.0(4)
C9A-C10-C9	27.8(2)	C10A-C10-H10A	114(2)
C9A-C10-H10A	100(2)	C9-C10-H10A	124(2)

C10A-C10-H10B	113.1(18)	C9A-C10-H10B	122.9(18)
C9-C10-H10B	101.4(18)	H10A-C10-H10B	100(3)
C14A-C10A-C11	124.6(2)	C14A-C10A-C10	111.4(2)
C11-C10A-C10	123.9(2)	C10A-C11-C12	112.9(2)
C10A-C11-H11A	108.5(14)	C12-C11-H11A	108.7(14)
C10A-C11-H11B	110.4(14)	C12-C11-H11B	108.1(15)
H11A-C11-H11B	108(2)	C13-C12-C11	120.2(3)
C13-C12-C15	60.74(18)	C11-C12-C15	119.1(2)
C13-C12-H12	117.3(13)	C11-C12-H12	113.2(14)
C15-C12-H12	116.8(14)	C12-C13-C14	121.1(3)
C12-C13-C15	60.88(18)	C14-C13-C15	117.3(3)
C12-C13-H13	114.4(13)	C14-C13-H13	117.7(13)
C15-C13-H13	112.8(13)	C14A-C14-C13	112.6(2)
C14A-C14-H14A	110.4(13)	C13-C14-H14A	107.9(13)
C14A-C14-H14B	111.0(15)	C13-C14-H14B	107.9(15)
H14A-C14-H14B	106.9(19)	C10A-C14A-C14	124.8(3)
C10A-C14A-C8	111.4(2)	C14-C14A-C8	123.8(2)
C16-C15-C13	117.2(3)	C16-C15-C12	118.8(3)
C13-C15-C12	58.38(17)	C16-C15-H15	117.1(15)
C13-C15-H15	116.7(14)	C12-C15-H15	115.7(15)
O1-C16-O2	122.8(2)	O1-C16-C15	123.2(3)
O2-C16-C15	114.0(3)		

5.11. 1, 3 Dibromo-azulene-6-carboxylic acid ethyl ester (113)



Molecular structure of **113**. For reason of better overview only one of both independent molecules was drawn

Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	a = 17032(2) nm
	b = 3969.4(5) nm
	c = 35819(5) nm
Volume, Z	2.4216(5) nm^3, 8

Bond lengths [A]

Br1-C1	1.881(5)	Br2-C3	1.882(5)
O1-C9	1.336(6)	O1-C10	1.460(6)
O2-C9	1.210(7)	C1-C2	1.374(8)
C1-C8A	1.413(7)	C2-C3	1.397(7)
C2-H2	0.9500	C3-C3A	1.398(7)
C3A-C4	1.376(7)	C3A-C8A	1.507(6)
C4-C5	1.399(8)	C4-H4	0.9500
C5-C6	1.410(8)	C5-H5	0.9500
C6-C7	1.394(7)	C6-C9	1.517(8)
C7-C8	1.388(8)	C7-H7	0.9500
C8-C8A	1.377(7)	C8-H8	0.9500
C10-C11	1.512(8)	C10-H10A	0.9900
C10-H10B	0.9900	C11-H11A	0.9800
C11-H11B	0.9800	C11-H11C	0.9800
Br1'-C1'	1.881(5)	Br2'-C3'	1.871(5)

O1'-C9'	1.338(7)	O1'-C10'	1.454(6)
O2'-C9'	1.206(7)	C1'-C8A'	1.386(7)
C1'-C2'	1.400(8)	C2'-C3'	1.409(7)
C2'-H2'	0.9500	C3'-C3A'	1.398(8)
C3A'-C4'	1.380(7)	C3A'-C8A'	1.495(7)
C4'-C5'	1.390(8)	C4'-H4'	0.9500
C5'-C6'	1.405(8)	C5'-H5'	0.9500
C6'-C7'	1.401(7)	C6'-C9'	1.510(7)
C7'-C8'	1.386(8)	C7'-H7'	0.9500
C8'-C8A'	1.388(8)	C8'-H8'	0.9500
C10'-C11'	1.497(8)	C10'-H10C	0.9900
C10'-H10D	0.9900	C11'-H11D	0.9800
C11'-H11E	0.9800	C11'-H11F	0.9800

Bond angles [°].

C9-O1-C10	116.4(4)	C2-C1-C8A	111.8(5)
C2-C1-Br1	125.2(4)	C8A-C1-Br1	123.0(4)
C1-C2-C3	107.6(5)	C1-C2-H2	126.2
C3-C2-H2	126.2	C2-C3-C3A	110.5(4)
C2-C3-Br2	124.5(4)	C3A-C3-Br2	125.0(4)
C4-C3A-C3	127.2(5)	C4-C3A-C8A	126.7(5)
C3-C3A-C8A	106.0(4)	C3A-C4-C5	130.0(5)
C3A-C4-H4	115.0	C5-C4-H4	115.0
C4-C5-C6	128.0(5)	C4-C5-H5	116.0
C6-C5-H5	116.0	C7-C6-C5	129.2(5)
C7-C6-C9	114.0(5)	C5-C6-C9	116.8(5)
C8-C7-C6	129.0(5)	C8-C7-H7	115.5
C6-C7-H7	115.5	C8A-C8-C7	129.6(5)
C8A-C8-H8	115.2	C7-C8-H8	115.2
C8-C8A-C1	128.6(5)	C8-C8A-C3A	127.3(5)
C1-C8A-C3A	104.1(4)	O2-C9-O1	123.6(5)
O2-C9-C6	123.8(5)	O1-C9-C6	112.6(5)
O1-C10-C11	106.1(4)	O1-C10-H10A	110.5
C11-C10-H10A	110.5	O1-C10-H10B	110.5
C11-C10-H10B	110.5	H10A-C10-H10B	108.7
C10-C11-H11A	109.5	C10-C11-H11B	109.5
H11A-C11-H11B	109.5	C10-C11-H11C	109.5
H11A-C11-H11C	109.5	H11B-C11-H11C	109.5

C9'-O1'-C10'	116.4(4)	C8A'-C1'-C2'	110.9(5)
C8A'-C1'-Br1'	126.0(4)	C2'-C1'-Br1'	122.9(4)
C1'-C2'-C3'	107.2(5)	C1'-C2'-H2'	126.4
C3'-C2'-H2'	126.4	C3A'-C3'-C2'	109.9(5)
C3A'-C3'-Br2'	125.4(4)	C2'-C3'-Br2'	124.6(4)
C4'-C3A'-C3'	126.8(5)	C4'-C3A'-C8A'	127.1(5)
C3'-C3A'-C8A'	106.1(4)	C3A'-C4'-C5'	129.3(5)
C3A'-C4'-H4'	115.4	C5'-C4'-H4'	115.4
C4'-C5'-C6'	129.3(5)	C4'-C5'-H5'	115.3
C6'-C5'-H5'	115.3	C7'-C6'-C5'	128.4(5)
C7'-C6'-C9'	113.5(5)	C5'-C6'-C9'	118.1(5)
C8'-C7'-C6'	129.1(5)	C8'-C7'-H7'	115.5
C6'-C7'-H7'	115.5	C7'-C8'-C8A'	129.4(5)
C7'-C8'-H8'	115.3	C8A'-C8'-H8'	115.3
C1'-C8A'-C8'	126.7(5)	C1'-C8A'-C3A'	105.8(5)
C8'-C8A'-C3A'	127.4(5)	O2'-C9'-O1'	123.6(5)
O2'-C9'-C6'	124.2(5)	O1'-C9'-C6'	112.2(4)
O1'-C10'-C11'	107.4(5)	O1'-C10'-H10C	110.2
C11'-C10'-H10C	110.2	O1'-C10'-H10D	110.2
C11'-C10'-H10D	110.2	H10C-C10'-H10D	108.5
C10'-C11'-H11D	109.5	C10'-C11'-H11E	109.5
H11D-C11'-H11E	109.5	C10'-C11'-H11F	109.5
H11D-C11'-H11F	109.5	H11E-C11'-H11F	

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